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(54) **Laundry and cleaning compositions**

(57) The present invention relates to a laundry and cleaning composition comprising a detergent ingredient and a product of reaction between a primary amine and a perfume component. By the present invention, there is obtained a release of the active component over a longer period of time than by the use of the active itself.

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## Description

Field of the invention

[0001] The present invention relates to laundry and cleaning compositions comprising a product of reaction between an amine and a perfume component, in particular aldehyde or ketone perfumes.

Background of the invention

[0002] Laundry and cleaning products are well-known in the art. However, consumer acceptance of laundry and cleaning products is determined not only by the performance achieved with these products but also by the aesthetics associated therewith. The perfume components are therefore an important aspect of the successful formulation of such commercial products.

[0003] It is also desired by consumers for laundered fabrics to maintain the pleasing fragrance over time. Indeed, perfume additives make laundry compositions more aesthetically pleasing to the consumer, and in some cases the perfume imparts a pleasant fragrance to fabrics treated therewith. However, the amount of perfume carried-over from an aqueous laundry bath onto fabrics is often marginal and does not last long on the fabric. Furthermore, fragrance materials are often very costly and their inefficient use in laundry and cleaning compositions and ineffective delivery to fabrics results in a very high cost to both consumers and laundry and cleaning manufacturers. Industry, therefore, continues to seek with urgency for more efficient and effective fragrance delivery in laundry and cleaning products, especially for improvement in the provision of long-lasting fragrance to the fabrics.

[0004] One solution is to use carrier mechanisms for perfume delivery, such as by encapsulation. This is taught in the prior art and described in U.S. 5,188,753.

[0005] Still another solution is to formulate compounds which provide a delayed release of the perfume over a longer period of time than by the use of the perfume itself. Disclosure of such compounds may be found in WO 95/04809, WO 95/08976 and co-pending application EP 95303762.9.

[0006] However, notwithstanding the advances in the art, there is still a need for a compound which provides a delayed release of the perfume component.

[0007] That need is even more acute for perfume ingredients which are characteristic of the fresh notes, namely the aldehydes and ketones perfume ingredients. Indeed, whilst these provide a fresh fragrance, these perfumes are also very volatile and have a low substantivity on the surface to be treated like fabrics.

[0008] Accordingly, it is a further object of the invention to provide a laundry and cleaning composition comprising a perfume component which provides a fresh fragrance and is substantive to the treated surface.

[0009] The Applicant has now found that specific reaction products of amine compounds with an active aldehyde or ketone, such as imines compounds, also provide a delayed release of the active such as a perfume.

[0010] Imine compounds are known in the art under the name of Schiff bases which is the condensation of an aldehyde perfume ingredient with an anthranilate. A typical description can be found in US 4853369. By means of this compound, the aldehyde perfume is made substantive to the fabrics. However, a problem encountered with these schiff bases is that the methylantranilate compound also exhibits a strong scent, which as a result produces a mixture of fragrances, thereby reducing or even inhibiting the aldehyde fragrance perception.

[0011] To achieve such perfume composition with comparable aldehyde or ketones fresh notes whilst still having satisfactory fabric substantivity, perfumers have formulated around the composition. For example, by having a carrier or encapsulating material for such notes such as with cyclodextrin, zeolites or starch.

[0012] Still another solution is the use of a glucosamine as described in JP 09040687. However, this compound has been found to give a very low stability in the wash/cleaning process. As a result, insufficient perfume residuality on the treated fabric and/or hard surface has been found with these glucosamine compounds.

[0013] A further solution is described in Chemical release control, Kamogawa et Al., J. Poly. Sci. . Polym. Chem. Ed. Vol 20, 3121 (1982) which describe the use of amino styrene compounds condensed with aldehydes perfumes, whereby the release of the perfume is triggered by means of copolymerisation or acidification of the compound. Its use in laundry and cleaning product is however not mentioned.

[0014] The Applicant has now found that a reaction product between a specific primary amine and a perfume component also fulfill such a need.

[0015] Another advantage of the compounds of the invention is their ease of manufacture rendering their use most desirable.

Summary of the invention

[0016] The present invention relates to a laundry and cleaning composition comprising a detergent ingredient and a product of reaction between a primary amine compound and a perfume component selected from ketone, aldehyde, and mixtures thereof, characterised in that said amine compound has an Odor Intensity Index of less than that of a 1% solution of methylantranilate in dipropylene glycol, and the product of reaction a Dry Surface Odor Index of more than 5.

[0017] In a further aspect of the invention, there is provided a method of delivering residual fragrance to a surface by means of the compound or composition of the invention.

**Detailed description of the invention****I-Product of reaction between a compound containing a primary amine functional group and a perfume component**

**[0018]** An essential component of the invention is a product of reaction between a compound containing a primary amine functional group and a perfume component, so called hereinafter "amine reaction product".

**A-Primary amine**

**[0019]** By "primary amine", it is meant a component which carries at least one primary amine and/or amide function.

**[0020]** The primary amine compound is also characterized by an Odor Intensity Index of less than that of a 1% solution of methylantranilate in dipropylene glycol.

**Odor Intensity Index method**

**[0021]** By Odor Intensity Index, it is meant that the pure chemicals were diluted at 1% in Dipropylene Glycol, odor-free solvent used in perfumery. This percentage is more representative of usage levels. Smelling strips, or so called "blotters", were dipped and presented to the expert panellist for evaluation. Expert panellists are assessors trained for at least six months in odor grading and whose gradings are checked for accuracy and reproducibility versus a reference on an on-going basis. For each amine compound, the panellist was presented two blotters: one reference (Me Anthranilate, unknown from the panellist) and the sample. The panellist was asked to rank both smelling strips on the 0-5 odor intensity scale, 0 being no odor detected, 5 being very strong odor present.

**Results:**

**[0022]** The following represents Odor Intensity Index of an amine compound suitable for use in the present invention and according to the above procedure. In each case, numbers are arithmetic averages among 5 expert panellists and the results are statistically significantly different at 95% confidence level:

Methylantranilate 1% (reference)	3.4
Ethyl-4-aminobenzoate (EAB) 1%	0.9

**[0023]** A general structure for the primary amine compound of the invention is as follows:

$B-(NH_2)_n$ ;

wherein B is a carrier material, and n is an index of value of at least 1.

**[0024]** Preferred B carriers are inorganic or organic carriers.

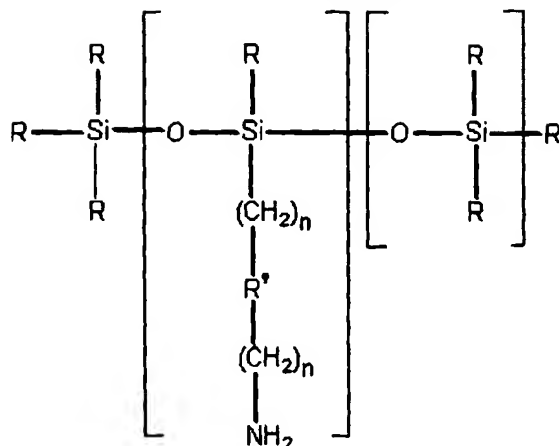
**[0025]** By "inorganic carrier", it is meant a carrier which is non- or substantially non carbon based backbones.

**[0026]** Among the inorganic carriers, preferred inorganic carriers are mono or polymers or organic-organosilicon copolymers of amino derivatised organo silane, siloxane, silazane, alumane, aluminum siloxane, or aluminum silicate compounds. Typical examples of such carriers are: organosiloxanes with at least one primary amine moiety like the diaminoalkylsiloxane  $[H_2NCH_2(CH_3)_2Si]_nO$ , or the organoaminosilane  $(C_6H_5)_3SiNH_2$  described in: Chemistry and Technology of Silicone, W. Noll, Academic Press Inc. 1998, London, pp 209, 106).

**[0027]** Mono or polymer or organic-organosilicon copolymers containing one or more organosilylhydrazine moiety are also preferred. A typical example of such a class of carrier material is the N,N'-bis(trimethylsilyl)hydrazine  $(Me_3Si)_2NNH_2$  described in: The OrganoSilicon Chemistry Second international Symposium, Pure and Applied Chemistry, Vol. 19 Nos 3-4, (1969).

**[0028]** The following are also preferred mono or poly silazanes and which are exemplified by the 1,1,1,3,3,3,-hexamethyl-2-phenyldiaminosilyldisilazane  $[(CH_3)_3Si]_2NSi(C_6H_5)NH_2$  2 described in: OrganoSilicon Compounds, 1965, V. Bazant and al. Academic Press). Still other preferred examples of polymer silicone derivatives are the cyclic 1,1,5,5,7,7,11,11-Octamethyl-3-9-bis-[2-(2-aminoethylamino)-ethyl]-1,5,7,11-tetrasiloxane-3,9-diaza-6,12-dioxacyclododecane and the Hexaethoxydiamino cyclotetrasiloxane  $(C_6H_5)(NH_2)_2Si_4O_4$ , id, Vol 2 part 2, p 474, p454).

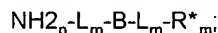
**[0029]** Preferred amino functionalized inorganic polymeric carriers for use herein are polyaminoalkyl polysiloxanes. Typical disclosure can be found in JP 79,131,096, and EP 058 493. Still other inorganic polymeric carriers suitable for use herein are the amino functionalized polydi-alkylsiloxanes, as described in EP 150 867 and having the general formula:



[0030] Wherein R = C<sub>1-16</sub> preferentially C<sub>1-4</sub> alkyl; n is an integer from 0 to 16 preferentially from 1 to 6, R' = nil, O, C=O, COO, NC=O, C=O-NR, NR, SO<sub>m</sub>, m = 2,3.

[0031] By organic carriers, it is meant carriers having essentially carbon bond backbones. Typical amines having organic carrier include aminoaryl derivatives, polyamines, aminoacids and derivatives, substituted amines and amides, glucamines, dendrimers and amino-substituted mono-, di-, oligo-, poly-saccharides.

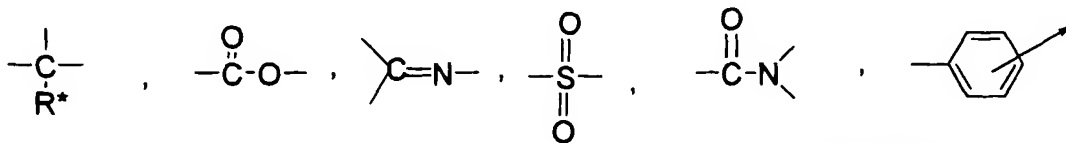
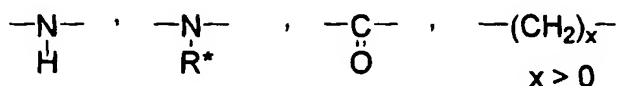
[0032] Of course, the amine compound can be interrupted or substituted by linkers or cellulose substantive group. A general formula for this amine compound may be represented as follows:



wherein each m is an index of value 0 or at least 1, and n is an index of value of at least 1 as defined herein before. As can be seen above, the amine group is linked to a carrier molecule as defined by classes hereinafter described. The primary amine group is either directly linked to the carrier group or via a linker group L. The carrier can also be substituted by a R\* substituent, and R\* can be linked to the carrier either directly or via a linker group L. Of course, R\* can also contain branching groups like e.g. tertiary amine and amide groups.

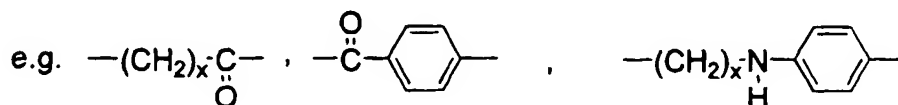
[0033] It is important for the purpose of the invention that the amine compound comprises at least one primary amine group to react with the perfume aldehyde and/or ketone to form the reaction products. Of course, the amine compound is not limited to having only one amine function. Indeed, more preferably, the amine compound comprises more than one amine function, thereby enabling the amine compound to react with several aldehydes and /or ketones. Accordingly, reaction products carrying mixed aldehyde(s) and/or ketone(s) can be achieved, thereby resulting in a mixed release of such fragrances.

[0034] Typical linker group include:



L can also be a combination

substitution in  
o, m, p - position



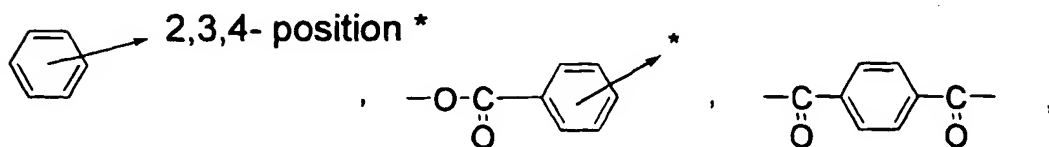
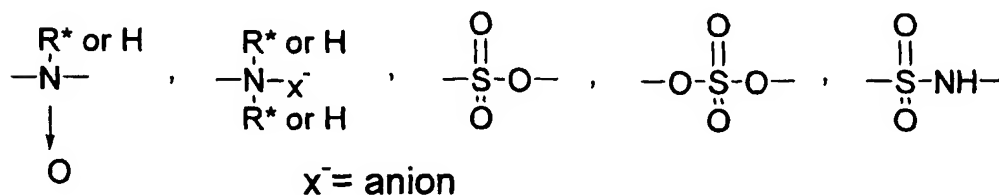
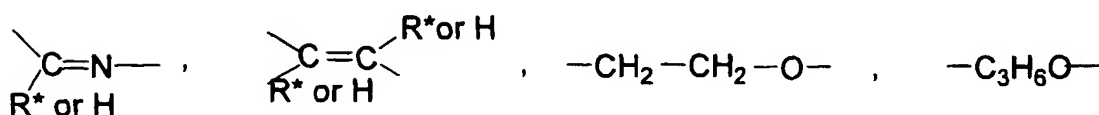
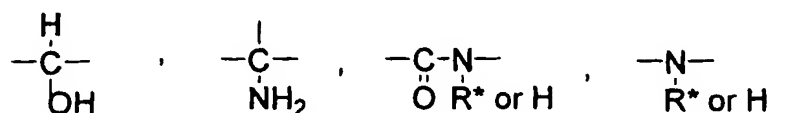
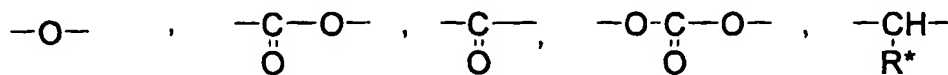
L can also contain —O— if this group is not directly linked to N  
e.g. H<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-O—

[0035] Most of the compounds described in the classes of amine compounds hereinafter will contain at least one substituent group classified as R\*.

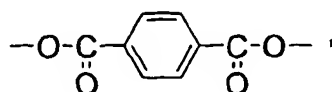
[0036] R\* contains 1 to 22 carbon atoms in the main chain and optionally can be an alkyl, alkenyl, or alkylbenzene chain. It can also contain alicyclic, aromatic, heteroaromatic or heterocyclic systems, either inserted into the main chain or by substitution of an H atom of the main chain. Further, R\* can either be linked to the carrier B material or via a linker L, as defined herein before. In this instance, L can also be -O-.

[0037] The main chain can contain from 1 to up to 15 R\* groups.

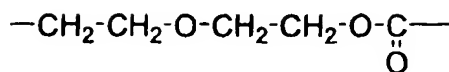
[0038] Typical R\* insertion groups include:



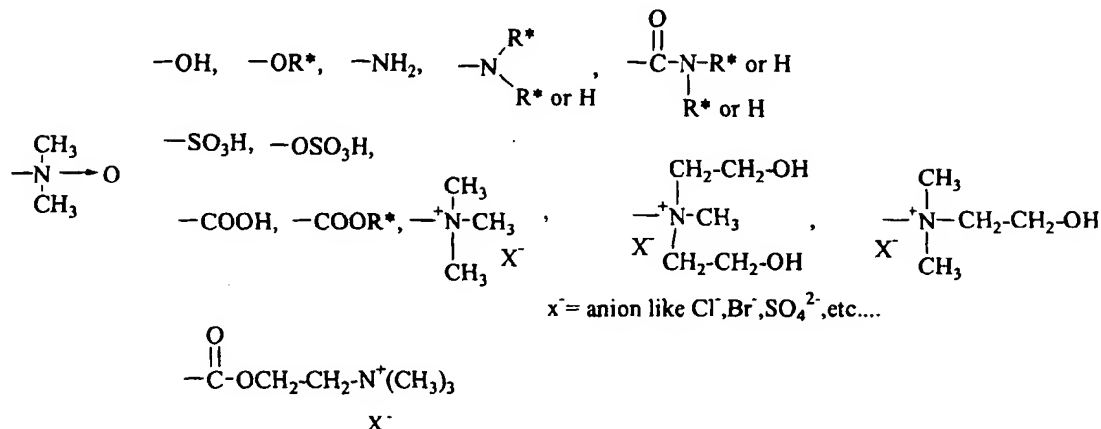
\* the arrow indicates upto 3 substitutions in position 2,3,4



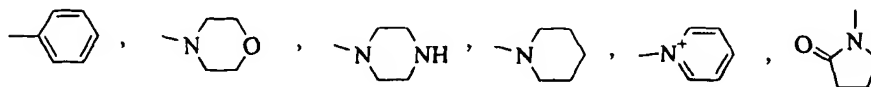
R\* can also contain several insertion groups linked together: e.g.  
e.g.:



[0039] Furthermore, R\* can carry a functional end group E that provides additional surface substantivity. Typical organic groups of this end group include:

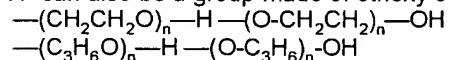


[0040] E can also be an aromatic, alicyclic, heteroaromatic, or heterocyclic group including mono-, di-, oligo-, polysaccharides



[0041] In addition, the R\*<sub>a</sub> group can also be modified via substitution of one or more H atoms in the main chain. The substitution group can either be E or the insertion groups as defined above where the insertion group is terminated by any of H, E, or R\*:

R\* can also be a group made of ethoxy or epoxy groups with n ranging from 1 to 15, including groups like:



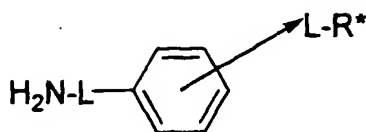
[0042] As defined herein before, preferred amine having organic carrier material B may be selected from aminoaryl derivatives, polyamines, aminoacids and derivatives, substituted amines and amides, glucamines, dendrimers, amino-substituted mono-, di-, oligo- polysaccharides and/or mixtures thereof.

#### 1-Amino aryl derivatives

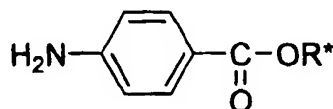
[0043] In this class of compounds, the amino group is preferably attached to a benzene ring. The benzene ring is further substituted in the para- and/or meta-position with R\* as defined herein before. R\* can be attached to the benzene ring via a linker L. The benzene ring can be substituted by other aromatic ring systems including naphtalene, indole, benzimidazole, pyrimidine, purine, and mixture thereof.

Preferably, the R\* is attached to the benzene ring in its para position.

[0044] Typical amino-benzene derivatives have the following formula:



[0045] Preferred amino-benzene derivatives have the following formula:



[0046] Preferred amino-benzene derivatives are alkyl esters of 4-amino benzoate compounds, preferably selected from ethyl-4-amino benzoate, phenylethyl-4-aminobenzoate, phenyl-4-aminobenzoate, 4-amino-N'-(3-aminopropyl)-benzamide, and mixtures thereof.

## 2-Polyamines

[0047] The polyamines of the invention need to have at least one, preferably more than one free and unmodified primary amine group, to react with the perfume aldehyde or ketone. In the polyamines, H can be substituted by  $\text{R}^*$ , optionally via a linker group L. Additionally, the primary amine group can be linked to the polymer end via a linker group L.

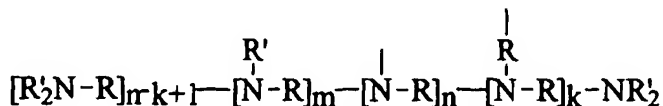
[0048] The polyamines compounds suitable for use in the present invention are water-soluble or dispersible, polyamines. Typically, the polyamines for use herein have a molecular weight between 150 and  $2 \times 10^6$ , preferably between 400 and  $10^6$ , most preferably between 5000 and  $10^6$ . These polyamines comprise backbones that can be either linear or cyclic. The polyamine backbones can also comprise polyamine branching chains to a greater or lesser degree. Preferably, the polyamine backbones described herein are modified in such a manner that at least one, preferably each nitrogen of the polyamine chain is thereafter described in terms of a unit that is substituted, quaternized, oxidized, or combinations thereof.

[0049] For the purposes of the present invention the term "modification" as it relates to the chemical structure of the polyamines is defined as replacing a backbone - NH hydrogen atom by an  $\text{R}'$  unit (substitution), quaternizing a backbone nitrogen (quaternized) or oxidizing a backbone nitrogen to the N-oxide (oxidized). The terms "modification" and "substitution" are used interchangeably when referring to the process of replacing a hydrogen atom attached to a backbone nitrogen with an  $\text{R}'$  unit. Quaternization or oxidation may take place in some circumstances without substitution, but substitution is preferably accompanied by oxidation or quaternization of at least one backbone nitrogen.

[0050] The linear or non-cyclic polyamine backbones that comprise the polyamine have the general formula:



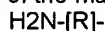
[0051] The cyclic polyamine backbones that comprise the polyamine have the general formula:



[0052] The above backbones prior to optional but preferred subsequent modification, comprise primary, secondary and tertiary amine nitrogens connected by R "linking" units

[0053] For the purpose of the present invention, primary amine nitrogens comprising the backbone or branching chain once modified are defined as V or Z "terminal" units. For example, when a primary amine moiety, located at the

end of the main polyamine backbone or branching chain having the structure

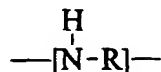


is modified according to the present invention, it is thereafter defined as a V "terminal" unit, or simply a V unit. However, for the purposes of the present invention, some or all of the primary amine moieties can remain unmodified subject to the restrictions further described herein below. These unmodified primary amine moieties by virtue of their position in the backbone chain remain "terminal" units. Likewise, when a primary amine moiety, located at the end of the main polyamine backbone having the structure



is modified according to the present invention, it is thereafter defined as a Z "terminal" unit, or simply a Z unit. This unit can remain unmodified subject to the restrictions further described herein below.

**[0054]** In a similar manner, secondary amine nitrogens comprising the backbone or branching chain once modified are defined as W "backbone" units. For example, when a secondary amine moiety, the major constituent of the backbones and branching chains of the present invention, having the structure



is modified according to the present invention, it is thereafter defined as a W "backbone" unit, or simply a W unit. However, for the purposes of the present invention, some or all of the secondary amine moieties can remain unmodified. These unmodified secondary amine moieties by virtue of their position in the backbone chain remain "backbone" units.

**[0055]** In a further similar manner, tertiary amine nitrogens comprising the backbone or branching chain once modified are further referred to as Y "branching" units. For example, when a tertiary amine moiety, which is a chain branch point of either the polyamine backbone or other branching chains or rings, having the structure



is modified according to the present invention, it is thereafter defined as a Y "branching" unit, or simply a Y unit. However, for the purposes of the present invention, some or all of the tertiary amine moieties can remain unmodified. These unmodified tertiary amine moieties by virtue of their position in the backbone chain remain "branching" units. The R units associated with the V, W and Y unit nitrogens which serve to connect the polyamine nitrogens, are described herein below.

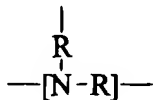
**[0056]** The final modified structure of the polyamines of the present invention can be therefore represented by the general formula



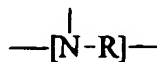
for linear polyamine and by the general formula



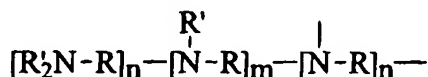
for cyclic polyamine. For the case of polyamines comprising rings, a Y' unit of the formula



serves as a branch point for a backbone or branch ring. For every Y' unit there is a Y unit having the formula



that will form the connection point of the ring to the main polymer chain or branch. In the unique case where the backbone is a complete ring, the polyamine backbone has the formula





therefore comprising no Z terminal unit and having the formula



wherein k is the number of ring forming branching units. Preferably the polyamine backbones of the present invention comprise no rings.

[0057] In the case of non-cyclic polyamines, the ratio of the index n to the index m relates to the relative degree of branching. A fully non-branched linear modified polyamine according to the present invention has the formula

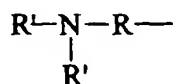


that is, n is equal to 0. The greater the value of n (the lower the ratio of m to n), the greater the degree of branching in the molecule. Typically the value for m ranges from a minimum value of 2 to 700, preferably 4 to 400, however larger values of m, especially when the value of the index n is very low or nearly 0, are also preferred.

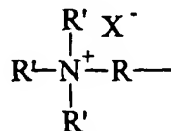
[0058] Each polyamine nitrogen whether primary, secondary or tertiary, once modified according to the present invention, is further defined as being a member of one of three general classes; simple substituted, quaternized or oxidized. Those polyamine nitrogen units not modified are classed into V, W, Y, Y' or Z units depending on whether they are primary, secondary or tertiary nitrogens. That is unmodified primary amine nitrogens are V or Z units, unmodified secondary amine nitrogens are W units or Y' units and unmodified tertiary amine nitrogens are Y units for the purposes of the present invention.

[0059] Modified primary amine moieties are defined as V "terminal" units having one of three forms:

a) simple substituted units having the structure:

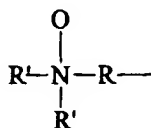


b) quaternized units having the structure:



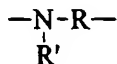
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

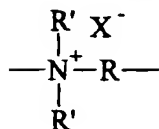


[0060] Modified secondary amine moieties are defined as W "backbone" units having one of three forms:

a) simple substituted units having the structure:

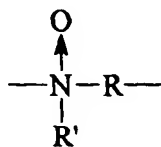


b) quaternized units having the structure:



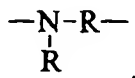
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

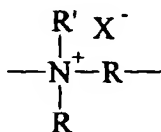


[0061] Other modified secondary amine moieties are defined as Y' units having one of three forms:

a) simple substituted units having the structure:

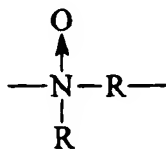


b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

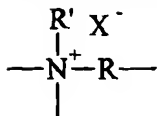


[0062] Modified tertiary amine moieties are defined as Y "branching" units having one of three forms:

a) unmodified units having the structure:

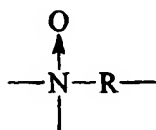


b) quaternized units having the structure:



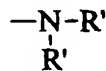
wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

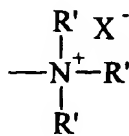


**[0063]** Certain modified primary amine moieties are defined as Z "terminal" units having one of three forms:

a) simple substituted units having the structure:

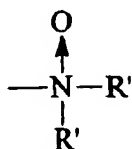


b) quaternized units having the structure:



wherein X is a suitable counter ion providing charge balance; and

c) oxidized units having the structure:

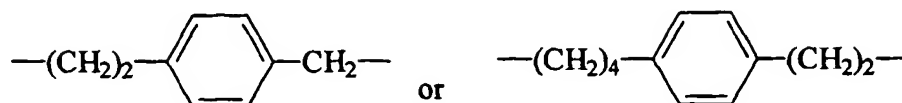


**[0064]** When any position on a nitrogen is unsubstituted or unmodified, it is understood that hydrogen will substitute for R'. For example, a primary amine unit comprising one R' unit in the form of a hydroxyethyl moiety is a V terminal unit having the formula (HOCH<sub>2</sub>CH<sub>2</sub>)HN-.

**[0065]** For the purposes of the present invention there are two types of chain terminating units, the V and Z units. The Z "terminal" unit derives from a terminal primary amino moiety of the structure -NH<sub>2</sub>. Non-cyclic polyamine backbones according to the present invention comprise only one Z unit whereas cyclic polyamines can comprise no Z units. The Z "terminal" unit can be substituted with any of the R' units described further herein below, except when the Z unit is modified to form an N-oxide. In the case where the Z unit nitrogen is oxidized to an N-oxide, the nitrogen must be modified and therefore R' cannot be a hydrogen.

**[0066]** The polyamines of the present invention comprise backbone R "linking" units that serve to connect the nitrogen atoms of the backbone. R units comprise units that for the purposes of the present invention are referred to as "hydrocarbyl R" units and "oxy R" units. The "hydrocarbyl" R units are C<sub>2</sub>-C<sub>12</sub> alkylene, C<sub>4</sub>-C<sub>12</sub> alkenylene, C<sub>3</sub>-C<sub>12</sub> hydroxyalkylene wherein the hydroxyl moiety may take any position on the R unit chain except the carbon atoms directly connected to the polyamine backbone nitrogens; C<sub>4</sub>-C<sub>12</sub> dihydroxyalkylene wherein the hydroxyl moieties may occupy any two of the carbon atoms of the R unit chain except those carbon atoms directly connected to the polyamine backbone nitrogens; C<sub>8</sub>-C<sub>12</sub> dialkylarylene which for the purpose of the present invention are arylene

moieties having two alkyl substituent groups as part of the linking chain. For example, a dialkylarylene unit has the formula



10 although the unit need not be 1,4-substituted, but can also be 1,2 or 1,3 substituted C2-C12 alkylene, preferably ethylene, 1,2-propylene, and mixtures thereof, more preferably ethylene. The "oxy" R units comprise - (R1O)<sub>x</sub>R5(OR1)<sub>x</sub>-, -CH<sub>2</sub>CH(OR<sub>2</sub>)CH<sub>2</sub>Oz(R1O)yR1(OCH<sub>2</sub>CH(OR<sub>2</sub>)CH<sub>2</sub>)w-, -CH<sub>2</sub>CH(OR<sub>2</sub>)CH<sub>2</sub>-, -(R1O)<sub>x</sub>R1-, and mixtures thereof. Preferred R units are selected from the group consisting of C2-C12 alkylene, C3-C12 hydroxyalkylene, C4-C12 dihydroxyalkylene, C8-C12 dialkylarylene, -(R1O)<sub>x</sub>R1-, -CH<sub>2</sub>CH(OR<sub>2</sub>)CH<sub>2</sub>-, -(CH<sub>2</sub>CH(OH)CH<sub>2</sub>O)z(R1O)yR1(OCH<sub>2</sub>CH(OH)CH<sub>2</sub>)w-, -(R1O)<sub>x</sub>R5(OR1)<sub>x</sub>-, more preferred R units are C2-C12 alkylene, C3-C12 hydroxyalkylene, C4-C12 dihydroxyalkylene, -(R1O)<sub>x</sub>R1-, -(R1O)<sub>x</sub>R5(OR1)<sub>x</sub>-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>Oz(R1O)yR1(OCH<sub>2</sub>CH(OH)CH<sub>2</sub>)w-, and mixtures thereof, even more preferred R units are C2-C12 alkylene, C3 hydroxyalkylene, and mixtures thereof most preferred are C2-C6 alkylene. The most preferred backbones of the present invention comprise at least 50% R units that are ethylene.

20 R1 units are C2-C6 alkylene, and mixtures thereof, preferably ethylene.

R2 is hydrogen, and -(R1O)<sub>x</sub>B, preferably hydrogen.

25 R3 is C1-C18 alkyl, C7-C12 arylalkylene, C7-C12 alkyl substituted aryl, C6-C12 aryl, and mixtures thereof, preferably C1-C12 alkyl, C7-C12 arylalkylene, more preferably C1-C12 alkyl, most preferably methyl. R3 units serve as part of R' units described herein below.

R4 is C1-C12 alkylene, C4-C12 alkenylene, C8-C12 arylalkylene, C6-C10 arylene, preferably C1-C10 alkylene, C8-C12 arylalkylene, more preferably C2-C8 alkylene, most preferably ethylene or butylene.

30 R5 is C1-C12 alkylene, C3-C12 hydroxyalkylene, C4-C12 dihydroxyalkylene, C8-C12 dialkylarylene, -C(O)-, -C(O)NHR6NHC(O)-, -C(O)(R4)rC(O)-, -R1(OR1)-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O(R1O)yR1OCH<sub>2</sub>CH(OH)CH<sub>2</sub>-, -C(O)(R4)rC(O)-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>-, R5 is preferably ethylene, -C(O)-, -C(O)NHR6NHC(O)-, -R1(OR1)-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>-, -CH<sub>2</sub>CH(OH)CH<sub>2</sub>O(R1O)yR1OCH<sub>2</sub>CH(OH)CH<sub>2</sub>-, more preferably -CH<sub>2</sub>CH(OH)CH<sub>2</sub>-.

R6 is C2-C12 alkylene or C6-C12 arylene.

35 **[0067]** The preferred "oxy" R units are further defined in terms of the R1, R2, and R5 units. Preferred "oxy" R units comprise the preferred R1, R2, and R5 units. The preferred polyamines of the present invention comprise at least 50% R1 units that are ethylene. Preferred R1, R2, and R5 units are combined with the "oxy" R units to yield the preferred "oxy" R units in the following manner.

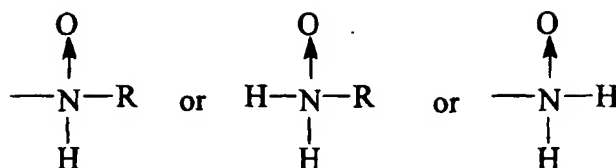
40 i) Substituting more preferred R5 into -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>R5(OCH<sub>2</sub>CH<sub>2</sub>)<sub>x</sub>- yields -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>x</sub>CH<sub>2</sub>CHOHCH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>x</sub>-.

ii) Substituting preferred R1 and R2 into -(CH<sub>2</sub>CH(OR<sub>2</sub>)CH<sub>2</sub>O)z-(R1O)yR1O(CH<sub>2</sub>CH(OR<sub>2</sub>)CH<sub>2</sub>)w- yields -(CH<sub>2</sub>CH(OH)CH<sub>2</sub>O)z-(CH<sub>2</sub>CH<sub>2</sub>O)yCH<sub>2</sub>CH<sub>2</sub>O(CH<sub>2</sub>CH(OH)CH<sub>2</sub>)w-.

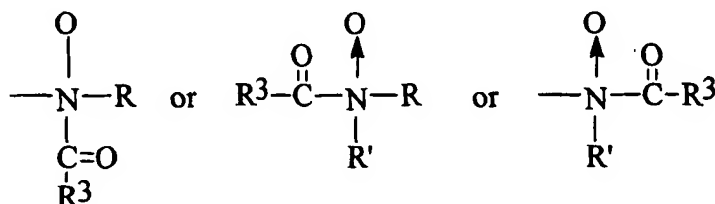
45 iii) Substituting preferred R2 into -CH<sub>2</sub>CH(OR<sub>2</sub>)CH<sub>2</sub>- yields -CH<sub>2</sub>CH(OH)CH<sub>2</sub>-.

50 R' units are selected from the group consisting of hydrogen, C1-C22 alkyl, C3-C22 alkenyl, C7-C22 arylalkyl, C2-C22 hydroxyalkyl, -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>SO<sub>3</sub>M, -CH(CH<sub>2</sub>CO<sub>2</sub>M)CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M, -(R1O)mB, -C(O)R3, preferably hydrogen, C2-C22 hydroxyalkylene, benzyl, C1-C22 alkylene, -(R1O)mB, -C(O)R3, -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>SO<sub>3</sub>M, -CH(CH<sub>2</sub>CO<sub>2</sub>M)CO<sub>2</sub>M, more preferably C1-C22 alkylene, -(R1O)<sub>x</sub>B, -C(O)R3, -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>SO<sub>3</sub>M, -CH(CH<sub>2</sub>CO<sub>2</sub>M)CO<sub>2</sub>M, most preferably C1-C22 alkylene, -(R1O)<sub>x</sub>B, and -C(O)R3. When no modification or substitution is made on a nitrogen then hydrogen atom will remain as the moiety representing R'. A most preferred R' unit is (R1O)<sub>x</sub>B.

55 **[0068]** R' units do not comprise hydrogen atom when the V, W or Z units are oxidized, that is the nitrogens are N-oxides. For example, the backbone chain or branching chains do not comprise units of the following structure:



[0069] Additionally, R' units do not comprise carbonyl moieties directly bonded to a nitrogen atom when the V, W or Z units are oxidized, that is, the nitrogens are N-oxides. According to the present invention, the R' unit -C(O)R<sup>3</sup> moiety is not bonded to an N-oxide modified nitrogen, that is, there are no N-oxide amides having the structure



or combinations thereof.

B is hydrogen, C1-C6 alkyl, -(CH<sub>2</sub>)<sub>q</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>M, -(CH<sub>2</sub>)<sub>q</sub>-(CHSO<sub>3</sub>M)CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>q</sub>-(CHSO<sub>2</sub>M)CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M, -PO<sub>3</sub>M, preferably hydrogen, -(CH<sub>2</sub>)<sub>q</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>q</sub>-(CHSO<sub>3</sub>M)CH<sub>2</sub>SO<sub>3</sub>M, -(CH<sub>2</sub>)<sub>q</sub>-(CHSO<sub>2</sub>M)CH<sub>2</sub>SO<sub>3</sub>M, more preferably hydrogen or -(CH<sub>2</sub>)<sub>q</sub>SO<sub>3</sub>M.

M is hydrogen or a water soluble cation in sufficient amount to satisfy charge balance. For example, a sodium cation equally satisfies -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>M, and -(CH<sub>2</sub>)<sub>q</sub>SO<sub>3</sub>M, thereby resulting in -(CH<sub>2</sub>)<sub>p</sub>CO<sub>2</sub>Na, and -(CH<sub>2</sub>)<sub>q</sub>SO<sub>3</sub>Na moieties. More than one monovalent cation, (sodium, potassium, etc.) can be combined to satisfy the required chemical charge balance. However, more than one anionic group may be charge balanced by a divalent cation, or more than one mono-valent cation may be necessary to satisfy the charge requirements of a poly-anionic radical. For example, a -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>M moiety substituted with sodium atoms has the formula -(CH<sub>2</sub>)<sub>p</sub>PO<sub>3</sub>Na<sub>3</sub>. Divalent cations such as calcium (Ca<sup>2+</sup>) or magnesium (Mg<sup>2+</sup>) may be substituted for or combined with other suitable mono-valent water soluble cations. Preferred cations are sodium and potassium, more preferred is sodium.

[0070] X is a water soluble anion such as chlorine (Cl<sup>-</sup>), bromine (Br<sup>-</sup>) and iodine (I<sup>-</sup>) or X can be any negatively charged radical such as sulfate (SO<sub>4</sub><sup>2-</sup>) and methosulfate (CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>).

[0071] The formula indices have the following values: p has the value from 1 to 6, q has the value from 0 to 6; r has the value 0 or 1; w has the value 0 or 1, x has the value from 1 to 100; y has the value from 0 to 100; z has the value 0 or 1; m has the value from 2 to 700, preferably from 4 to 400, n has the value from 0 to 350, preferably from 0 to 200; m + n has the value of at least 5. Preferably x has a value lying in the range of from 1 to 20, preferably from 1 to 10.

[0072] The preferred polyamines of the present invention comprise polyamine backbones wherein less than 50% of the R groups comprise "oxy" R units, preferably less than 20%, more preferably less than 5%, most preferably the R units comprise no "oxy" R units.

[0073] The most preferred polyamines which comprise no "oxy" R units comprise polyamine backbones wherein less than 50% of the R groups comprise more than 3 carbon atoms. For example, ethylene, 1,2-propylene, and 1,3-propylene comprise 3 or less carbon atoms and are the preferred "hydrocarbyl" R units. That is when backbone R units are C<sub>2</sub>-C<sub>12</sub> alkylene, preferred is C<sub>2</sub>-C<sub>3</sub> alkylene, most preferred is ethylene.

[0074] The polyamines of the present invention comprise modified homogeneous and non-homogeneous polyamine backbones, wherein 100% or less of the -NH units are modified. For the purpose of the present invention the term "homogeneous polyamine backbone" is defined as a polyamine backbone having R units that are the same (i.e., all ethylene). However, this sameness definition does not exclude polyamines that comprise other extraneous units comprising the polymer backbone which are present due to an artifact of the chosen method of chemical synthesis. For example, it is known to those skilled in the art that ethanolamine may be used as an "initiator" in the synthesis of polyethyleneimines, therefore a sample of polyethyleneimine that comprises one hydroxyethyl moiety resulting from the polymerization "initiator" would be considered to comprise a homogeneous polyamine backbone for the purposes of the present invention. A polyamine backbone comprising all ethylene R units wherein no branching Y units are present is a homogeneous backbone. A polyamine backbone comprising all ethylene R units is a homogeneous backbone regardless of the degree of branching or the number of cyclic branches present.

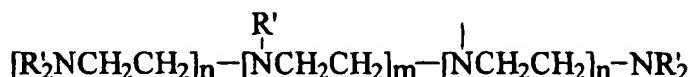
[0075] For the purposes of the present invention the term "non-homogeneous polymer backbone" refers to polyamine backbones that are a composite of various R unit lengths and R unit types. For example, a non-homogeneous backbone comprises R units that are a mixture of ethylene and 1,2-propylene units. For the purposes of

the present invention a mixture of "hydrocarbyl" and "oxy" R units is not necessary to provide a non-homogeneous backbone.

[0076] Preferred polyamines of the present invention comprise homogeneous polyamine backbones that are totally or partially substituted by polyethyleneoxy moieties, totally or partially quaternized amines, nitrogens totally or partially oxidized to N-oxides, and mixtures thereof. However, not all backbone amine nitrogens must be modified in the same manner, the choice of modification being left to the specific needs of the formulator. The degree of ethoxylation is also determined by the specific requirements of the formulator.

[0077] The preferred polyamines that comprise the backbone of the compounds of the present invention are generally polyalkyleneamines (PAI's), preferably polyethyleneamines (PEI's), or PEI's connected by moieties having longer R units than the parent PAI's or PEI's.

[0078] Preferred amine polymer backbones comprise R units that are C2 alkylene (ethylene) units, also known as polyethylenamines (PEI's). Preferred PEI's have at least moderate branching, that is the ratio of m to n is less than 4:1, however PEI's having a ratio of m to n of 2:1 are most preferred. Preferred backbones, prior to modification have the general formula:



wherein R', m and n are the same as defined herein above. Preferred PEI's will have a molecular weight greater than 200 daltons.

[0079] The relative proportions of primary, secondary and tertiary amine units in the polyamine backbone, especially in the case of PEI's, will vary, depending on the manner of preparation. Each hydrogen atom attached to each nitrogen atom of the polyamine backbone chain represents a potential site for subsequent substitution, quaternization or oxidation.

[0080] These polyamines can be prepared, for example, by polymerizing ethyleneimine in the presence of a catalyst such as carbon dioxide, sodium bisulfite, sulfuric acid, hydrogen peroxide, hydrochloric acid, acetic acid, etc. Specific methods for preparing these polyamine backbones are disclosed in U.S. Patent 2,182,306, Ulrich et al., issued December 5, 1939; U.S. Patent 3,033,746, Mayle et al., issued May 8, 1962; U.S. Patent 2,208,095, Esselmann et al., issued July 16, 1940; U.S. Patent 2,806,839, Crowther, issued September 17, 1957; and U.S. Patent 2,553,696, Wilson, issued May 21, 1951; all herein incorporated by reference.

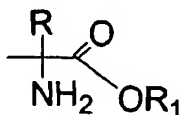
[0081] Preferred polyamines are polyethylenamines commercially available under the tradename Lupasol like Lupasol FG, G20,wfv, PR8515, WF, FC, G20, G35, G100, HF, P, PS, SK, SNA.

Still other polyamine suitable for use in the present invention are poly[oxy(methyl-1,2-ethanediyl)],  $\alpha$ -(2-aminomethylethyl)- $\omega$ -(2-aminomethyl-ethoxy)- (= C.A.S. No. 9046-10-0); poly[oxy(methyl-1,2-ethanediyl)],  $\alpha$ -hydro- $\omega$ -(2-aminomethylethoxy)-, ether with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (= C.A.S. No. 39423-51-3); commercially available under the tradename Jeffamines T-403, D-230, D-400, D-2000; 2,2',2"-triaminotriethylamine; 2,2'-diamino-diethylamine; 3,3'-diamino-dipropylamine, 1,3 bis aminoethyl-cyclohexane commercially available from Mitsubishi and the C12 Sternamines commercially available from Clariant like the C12 Sternamin(propylenamine)<sub>n</sub> with n=3/4, and mixtures thereof.

### 3-Amino acids and derivatives

[0082] Still other suitable compounds for use in the present invention are amino acids and their derivatives, especially ester and amide derivatives. More preferred compounds are those providing enhanced surface substantivity due to its structural feature. For clarification, the term amino acids and derivatives does not encompass polymeric compounds.

[0083] Suitable amino acids have the following functionality of formula:



[0084] Wherein R<sub>1</sub> = H, R\* or (L)-R\* and R is the amino acid side group, generally referred to as the "R group" such as in "Principles of Biochemistry" by Lehninger et al., 1997, Second Edition, Worth, pp114-116.

Preferred amino acids for use herein are selected tyrosine, tryptophane, lysine, glutamic acid, glutamine, aspartic acid, arginine, asparagine, phenylalanine, proline, glycine, serine, histidine, threonine, methionine, and mixture thereof, most preferably selected from tyrosine, tryptophane, and mixture thereof.

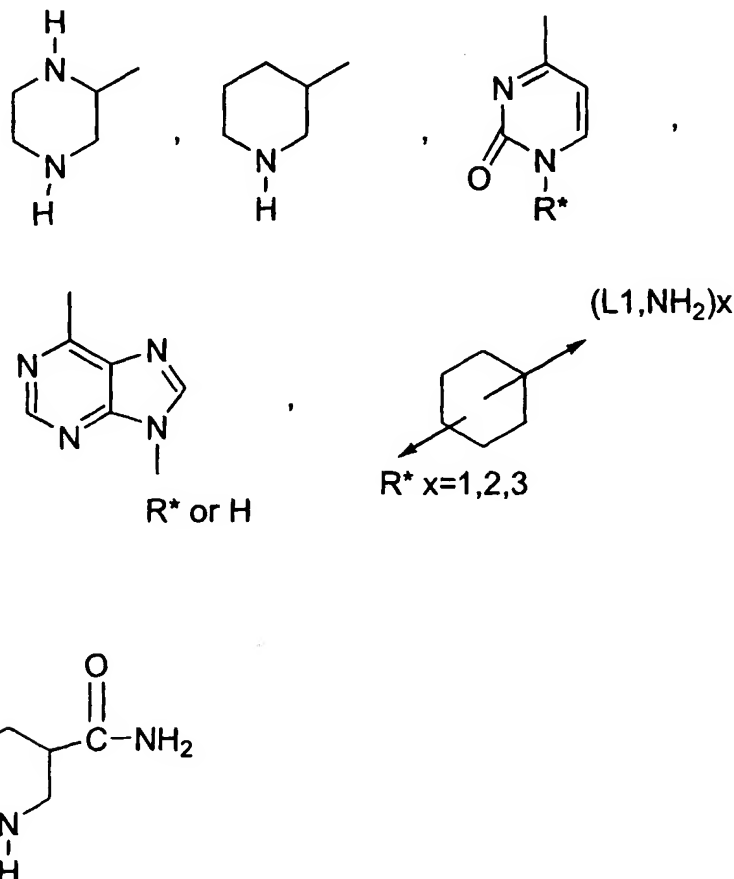
[0085] Still other preferred compound are the amino acid derivatives selected from tyrosine ethylate, glycine methylate, tryptophane ethylate, and mixture thereof.

4-Substituted amines and amides

[0086] For clarification, the term substituted amines and amides does not encompass polymeric compounds. Substituted amine and amide compounds suitable for use herein have the following general formula:  
 $\text{NH}_2\text{-L-R}^{**}$ , in which L is -CO- in case of an amide.

[0087] Other optional linker group may be as defined under R\*.

R\*\* is as defined herein before under R\* with the proviso that it contains at least 6 carbon atoms and/or N atoms and/or cyclohexyl-, piperidine, piperazine, and other heterocyclic groups like:



Optionally, H in NH can be substituted by R\*.

[0088] Preferred substituted amines and amides for use herein are selected from nipecotamide, N-coco-1,3-propenediamine; N-oley-1,3-propenediamine; N-(tallow alkyl)-1,3-propenediamine; 1,4-diamino cyclohexane; 1,2-diamino-cyclohexane; 1,12-diaminododecane, and mixtures thereof.

5-Glucamines

[0089] Still a further preferred class of amine compounds is the class of glucamines of general structure:

$\text{NH}_2\text{-CH}_2\text{-(CH(OH))}_x\text{-CH}_2\text{OH}$ , wherein one or several OH-function can be substituted, preferably by -OR\*, and wherein x is an integer of value 3 or 4. R\* can be linked to the OH groups either directly or via linker unit as mentioned herein before under L.

[0090] For clarification, the term glucamine does not encompass polymeric compounds.

[0091] Preferred compound of this class are selected from 2,3,4,5,6-pentamethoxy-glucamine; 6-acetylglucamine, glucamine, and mixture thereof.

6-Dendrimers

[0092] Another further class of amine compounds is the class of dendrimers. Suitable dendrimers carry free primary amine groups at the periphery of the spherical molecules, that can be reacted with (perfume) aldehydes or ketones to form the desired amine reaction product (perfume component) of the invention.

[0093] By dendrimers it is understood that the molecule is built up from a core molecule as described e.g. in WO 96/02588, in Synthesis, Feb. 1978, p. 155-158 or in Encyclopedia of Polymer Science & Engineering, 2<sup>nd</sup> ed.,

Hedstrand et al., in particular pages 46-91. The core is typically connected to multifunctional components to build up the "generations". For the purpose of the present invention, the nature of the inner generations is not critical. They can be based on e.g. polyamidoamines, polyamidoalcohols, polyethers, polyamides, polyethylenimines, etc. Important for the purpose of the present invention is that the outer generation(s) contain accessible primary amino functions.

**[0094]** Also suitable are the glyco dendrimers as described in e.g. Nachrichten aus Chemie 11 (1996), p. 1073-1079 and in WO 97/48711 provided that free primary amine groups are present at the surface of these molecules.

**[0095]** Preferred compounds are the polyethylenimine and/or polypropylenimine dendrimers, the commercially available Starburst® polyamidoamines (PAMAM) dendrimers, generation G0-G10 from Dendritech and the dendrimers Astromols®, generation 1-5 from DSM being DiAminoButane PolyAmine DAB (PA)<sub>x</sub> dendrimers with  $x = 2^0$  to  $2^4$  and  $n$  being generally comprised between 0 and 4.

#### 7-Amino-substituted mono-, di-, oligo-, poly-saccharides

**[0096]** Also suitable for the purpose of the present invention are specific amino-substituted mono-, di-, oligo-, poly-saccharides.

**[0097]** For the amino-substituted mono-saccharide of the present invention, it is necessary that the hemi-acetal and/or hemi-ketal functionality is blocked via a suitable substituent to provide sufficient stability for the intended application. As indicated here above, glucoseamine is not a suitable amine. However, if the hemi-acetal OH function is substituted by R\*, said monosaccharide becomes suitable for the purpose of the present invention. The amino group can be in position 2 to 5 or 6 depending on the type of monosaccharide and is preferably in C2, C5 or C6 position. Suitable amino-substituted mono-saccharides are:

- C5 aldosen/ketosen : ribose, arabinose, xylose, lyxose, ribulose, xylulose;
- C6 aldosen/ketosen : allose, altrose, glucose, mannose, gulose, idose, galactose, talose, fructose, sorbose, tagatose, psicose.

**[0098]** For amino-substituted di-saccharides with non-substituted aldose or ketose groups, the free OH-group needs to be substituted by R\*, e.g. in lactose and maltose, whereas in sucrose there is no free acetal/ketal OH group. Optionally, more than one OH group can be substituted by R\*. Suitable amino-substituted di-saccharides are amino substituted lactose, maltose, sucrose, cellobiose and trehalose.

**[0099]** Suitable amino-substituted oligo-, poly-saccharides are amino-substituted starch, cyclodextrin, dextran, glycogen, cellulose, mannan, guaran, levan, alternan glucose, mannose, galactose, fructose, lactose, maltose, sucrose, cellobiose, cyclodextrin, chitosan, and/or mixtures thereof. The molecules need to carry at least 1, preferably several, amino groups. Chitosan does not require additional amino substitution.

**[0100]** Also suitable for coupling carboxyl- or aldehyde-containing compounds are the following functionalised oligo-, poly-saccharides & glycans commercially available from the company Carbomer. Please find in brackets the reference number from Carbomer :

Amino alginate (5,00002), Diamino alginate (5,00003), Hexanediamine alginate (5,00004 - 5,00006 - 5,00008), dodecanediamine alginate (5,00005 - 5,00007 - 5,00009), 6-amino-6-deoxy cellulose (5,00020), O-ethylamine cellulose (5,00022), O-methylamine cellulose (5,00023), 3-amino-3-deoxy cellulose (5,00024), 2-amino-2 deoxy cellulose (5,00025), 2,3-diamino-2,3-dideoxy cellulose (5,00026), 6-[N-(1,6-hexanediamine)]-6-deoxy cellulose (5,00027), 6-[N-(1,12-dodecanediamine)]-6-deoxy cellulose (5,00028), O-[methyl-(N-1,6-hexanediamine)] cellulose (5,00029), O-[methyl-(N-1,12-dodecanediamine)] cellulose (5,00030), 2,3-di-(N-(1,12-dodecanediamine)] cellulose (5,00031), 2,3-diamino-2,3-deoxy alpha-cyclodextrin (5,00050), 2,3-diamino-2,3-deoxy beta-cyclodextrin (5,00051), 2,3-diamino-2,3-deoxy gamma-cyclodextrin (5,00052), 6-amino-6-deoxy alpha-cyclodextrin (5,00053), 6-amino-6-deoxy beta-cyclodextrin (5,00054), O-ethyleamino beta-cyclodextrin (5,00055), 6[N-(1,6-hexanediamino)-6-deoxy alpha cyclodextrin (5,00056), 6[N-(1,6-hexanediamino)-6-deoxy beta cyclodextrin (5,00057), Amino dextran (5,00060), N-[di-(1,6-hexanediamine)] dextran (5,00061), N-[di-(1,12-dodecanediamine)] dextran (5,00062), 6-amino-6-deoxy-alpha-D-galactosyl-guaran (5,00070), O-ethylamino guaran (5,00071), Diamino guaran (5,00072), 6-amino-6-deoxy-starch (5,00080), O-ethylamino starch (5,00081), 2,3-diamine-2,3-dideoxy starch (5,00082), N-[6-(1,6-hexanediamine)]-6-deoxy starch (5,00083), N-[6-(1,12-dodecanediamine)]-6-deoxy starch (5,00084) and 2,3-di-[N-(1,6-hexanediamine)]-2,3-dideoxy starch (5,00085)

#### B-Perfume

**[0101]** Preferably, for the above mentioned compounds, by perfume ketone or active aldehyde, it is meant any chain containing at least 1 carbon atom, preferably at least 5 carbon atoms.

**[0102]** A typical disclosure of suitable ketone and/or aldehydes, traditionally used in perfumery, can be found in "perfume and Flavor Chemicals", Vol. I and II, S. Arctander, Allured Publishing, 1994, ISBN 0-931710-35-5.

**[0103]** Perfume ketones components include components having odoriferous properties.

**[0104]** Preferably, for the above mentioned compounds, the perfume ketone is selected for its odor character from buccoxime; iso jasmone; methyl beta naphthyl ketone; musk indanone; tonalid/musk plus; Alpha-Damascone, Beta-Damascone, Delta-Damascone, Iso-Damascone, Damascenone, Damarose, Methyl-Dihydrojasmonate,



Menthone, Carvone, Camphor, Fenchone, Alpha-Ionone, Beta-Ionone, Gamma-Methyl so-called Ionone, Fleuramone, Dihydrojasmonone, Cis-Jasmonone, Iso-E-Super, Methyl- Cedrenyl-ketone or Methyl- Cedrylone, Acetophenone, Methyl-Acetophenone, Para-Methoxy-Acetophenone, Methyl-Beta-Naphtyl-Ketone, Benzyl-Acetone, Benzophenone, Para-Hydroxy-Phenyl-Butanone, Celery Ketone or Livescone, 6-Isopropyldecahydro-2-naphthone, Dimethyl-Octenone, Freskomenthe, 4-(1-Ethoxyvinyl)-3,3,5,5-tetramethyl-Cyclohexanone, Methyl-Heptenone, 2-(2-(4-Methyl-3-cyclohexen-1-yl)propyl)-cyclopentanone, 1-(p-Menthen-6(2)-yl)-1-propanone, 4-(4-Hydroxy-3-methoxyphenyl)-2-butanone, 2-Acetyl-3,3-Dimethyl-Norbornane, 6,7-Dihydro-1,1,2,3,3-Pentamethyl-4(5H)-Indanone, 4-Damascol, Dulcinyol or Cassione, Gelsone, Hexalon, Isocyclemonone E, Methyl Cyclocitronone, Methyl-Lavender-Ketone, Orivon, Para-tertiary-Butyl-Cyclohexanone, Verdone, Delphone, Muscone, Neobutenone, Plicatone, Veloutone, 2,4,4,7-Tetramethyloct-6-en-3-one, Tetrameran.

**[0105]** Preferably, for the above mentioned compounds, the preferred ketones are selected from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-Ionone, Iso-E-Super, 2,4,4,7-Tetramethyloct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damascenone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof.

**[0106]** Perfume aldehyde components include components having odoriferous properties.

**[0107]** Preferably, for the above mentioned compounds, the perfume aldehyde is selected for its odor character from adoxal; anisaldehyde; cymal; ethyl vanillin; florhydral; helional; heliotropin; hydroxycitronellal; koavone; lauric aldehyde; lyral; methyl nonyl acetaldehyde; P. T. buccinal; phenyl acetaldehyde; undecylenic aldehyde; vanillin; 2,6,10-trimethyl-9-undecenal, 3-dodecen-1-al, alpha-n-amyln cinnamic aldehyde, 4-methoxybenzaldehyde, benzaldehyde, 3-(4-tert butylphenyl)-propanal, 2-methyl-3-(para-methoxyphenyl) propanal, 2-methyl-4-(2,6,6-trimethyl-2(1)-cyclohexen-1-yl) butanal, 3-phenyl-2-propenal, cis-/trans-3,7-dimethyl-2,6-octadien-1-al, 3,7-dimethyl-6-octen-1-al, [(3,7-dimethyl-6-octenyl)oxy] acetaldehyde, 4-isopropylbenzaldehyde, 1,2,3,4,5,6,7,8-octahydro-8,8-dimethyl-2-naphthaldehyde, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde, 2-methyl-3-(isopropylphenyl)propanal, 1-decanal; decyl aldehyde, 2,6-dimethyl-5-heptenal, 4-(tricyclo[5.2.1.0(2,6)]-decylidene-8)-butanal, octahydro-4,7-methano-1H-indenecarboxaldehyde, 3-ethoxy-4-hydroxy benzaldehyde, para-ethyl-alpha, alpha-dimethyl hydrocinnamaldehyde, alpha-methyl-3,4-(methylenedioxy)-hydrocinnamaldehyde, 3,4-methylenedioxybenzaldehyde, alpha-n-hexyl cinnamic aldehyde, m-cymene-7-carboxaldehyde, alpha-methyl phenyl acetaldehyde, 7-hydroxy-3,7-dimethyl octanal, Undecenal, 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde, 4-(3)(4-methyl-3-pentenyl)-3-cyclohexen-carboxaldehyde, 1-dodecanal, 2,4-dimethyl cyclohexene-3-carboxaldehyde, 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde, 7-methoxy-3,7-dimethyloctan-1-al, 2-methyl undecanal, 2-methyl decanal, 1-nonanal, 1-octanal, 2,6,10-trimethyl-5,9-undecadienal, 2-methyl-3-(4-tertbutyl)propanal, dihydrocinnamic aldehyde, 1-methyl-4-(4-methyl-3-pentenyl)-3-cyclohexene-1-carboxaldehyde, 5 or 6 methoxy-4,7-methanoindan-1 or 2-carboxaldehyde, 3,7-dimethyloctan-1-al, 1-undecanal, 10-undecen-1-al, 4-hydroxy-3-methoxy benzaldehyde, 1-methyl-3-(4-methylpentyl)-3-cyclohexenecarboxaldehyde, 7-hydroxy-3,7-dimethyl-octanal, trans-4-decenal, 2,6-nonadienal, para-tolylacetaldehyde, 4-methylphenylacetaldehyde, 2-methyl-4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-2-butenal, ortho-methoxycinnamic aldehyde, 3,5,6-trimethyl-3-cyclohexene carboxaldehyde, 3,7-dimethyl-2-methylene-6-octenal, phenoxyacetaldehyde, 5,9-dimethyl-4,8-decadienal, peony aldehyde (6,10-dimethyl-3-oxa-5,9-undecadien-1-al), hexahydro-4,7-methanoindan-1-carboxaldehyde, 2-methyl octanal, alpha-methyl-4-(1-methyl ethyl) benzene acetaldehyde, 6,6-dimethyl-2-norpinene-2-propionaldehyde, para methyl phenoxy acetaldehyde, 2-methyl-3-phenyl-2-propen-1-al, 3,5,5-trimethyl hexanal, Hexahydro-8,8-dimethyl-2-naphthaldehyde, 3-propyl-bicyclo[2.2.1]-hept-5-ene-2-carbaldehyde, 9-decenal, 3-methyl-5-phenyl-1-pentanal, methylnonyl acetaldehyde, hexanal, trans-2-hexenal, 1-p-menthene-q-carboxaldehyde and mixtures thereof.

**[0108]** Most preferred aldehydes are selected from 1-decanal, benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadienal; alpha-n-amyln cinnamic aldehyde, alpha-n-hexyl cinnamic aldehyde, P.T. Buccinal, lyral, cymal, methyl nonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof.

**[0109]** In the above list of perfume ingredients, some are commercial names conventionally known to one skilled in the art, and also includes isomers. Such isomers are also suitable for use in the present invention.

**[0110]** In another embodiment, especially suitable for the purpose of the present invention are the perfume compounds, preferably the perfume ketones or active aldehydes, characterised by having a low Odor Detection Threshold. Such Odor Detection Threshold (ODT) should be lower than or equal to 1ppm, preferably lower than or equal to 10ppb - measured at controlled Gas Chromatography (GC) conditions such as described here below. This parameter refers to the value commonly used in the perfumery arts and which is the lowest concentration at which significant detection takes place that some odorous material is present. Please refer for example in "Compilation of Odor and Taste Threshold Value Data (ASTM DS 48 A)", edited by F. A. Fazzalari, International Business Machines, Hopwell Junction, NY and in Calkin et al., Perfumery, Practice and Principles, John Wiley & Sons, Inc., page 243 et seq (1994). For the purpose of the present invention, the Odor Detection Threshold is measured according to the following method: The gas chromatograph is characterized to determine the exact volume of material injected by the syringe, the precise split ratio, and the hydrocarbon response using a hydrocarbon standard of known concentration and chain-length distribution. The air flow rate is accurately measured and, assuming the duration of a human inhalation to last 0.02 minutes, the sampled volume is calculated. Since the precise concentration at the detector at any point in time is known, the mass per volume inhaled is known and hence the concentration of material. To determine the ODT of a perfume material, solutions are delivered to the sniff port at the back-calculated concentration. A panelist sniffs the GC effluent and identifies the retention time when odor is noticed. The average over all panelists determines the threshold of noticeability. The necessary amount of analyte is injected onto the column to achieve a certain concentration, such as 10 ppb, at the detector. Typical gas chromatograph parameters for determining odor

detection thresholds are listed below.

GC: 5890 Series II with FID detector

7673 Autosampler

Column: J&W Scientific DB-1

Length 30 meters ID 0.25 mm film thickness 1 micron

Method:

Split Injection: 17/1 split ratio

Autosampler: 1.13 microliters per injection

Column Flow: 1.10 mL/minute

Air Flow: 345 mL/minute

Inlet Temp. 245°C

Detector Temp. 285°C

Temperature Information

Initial Temperature: 50°C

Rate: 5C/minute

Final Temperature: 280°C

Final Time: 6 minutes

Leading assumptions: 0.02 minutes per sniff

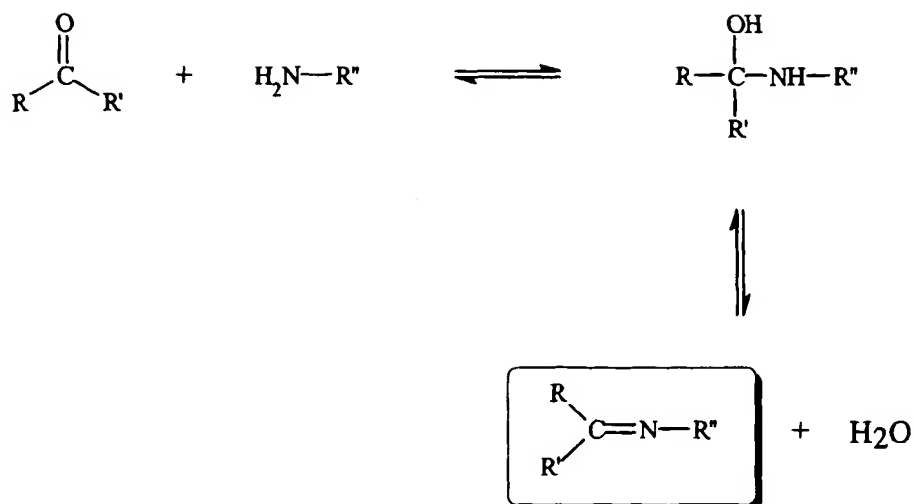
GC air adds to sample dilution

**[0111]** Examples of such preferred perfume components are those selected from : 2-methyl-2-(para-isopropylphenyl)-propionaldehyde, 1-(2,6,6-trimethyl-2-cyclo-hexan-1-yl)-2-buten-1-one and/or para-methoxyacetophenone. Even more preferred are the following compounds having an ODT  $\leq 10$ ppb measured with the method described above : undecylenic aldehyde, undecalactone gamma, heliotropin, dodecalactone gamma, p-anisic aldehyde, para hydroxy-phenyl-butanone, cymal, benzyl acetone, ionone alpha, p.t.bucinal, damascenone, ionone beta and methyl-nonyl ketone.

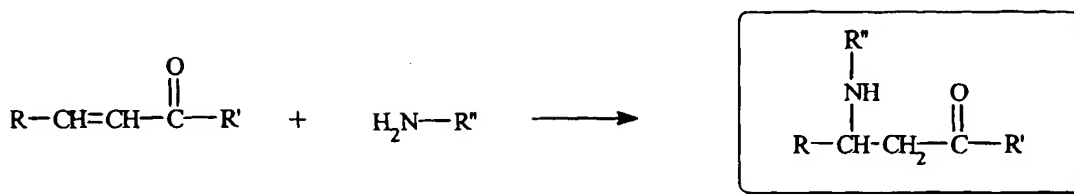
#### Process

**[0112]** Preparation of the component is made as follows in the Synthesis Examples. In general, the nitrogen analogs of ketones and aldehydes are called azomethines, Schiff bases or the more preferred name imines. These imines can easily be prepared by condensation of primary amines and carbonyl compounds by elimination of water.

**[0113]** A typical reaction profile is as follows:



$\alpha,\beta$ -Unsaturated ketones do not only condense with amines to form imines, but can also undergo a competitive 1,4-addition to form  $\beta$ -aminoketones.



**[0114]** By means of this simple method, compound and composition containing said compounds are made which achieve a delayed release of the active ingredient.

**[0115]** As can be observed, the perfume ingredient is typically present in equimolar amount to the amine function so as to enable the reaction to take place and provide the resulting amine reaction product. Of course, higher amount are not excluded and even preferred when the amine compound comprises more than one amine function. When the amine compound has more than one free primary amine group, several different perfume raw materials can be linked to the amine compound.

#### Mechanism of release

**[0116]** By the present invention, a delayed release of a perfume ingredient, i.e. ketone or aldehyde is obtained. Not to be bound by theory, the release is believed to occur by the following mechanisms:

**[0117]** For imine compounds, the perfume components are released upon breaking down of the imine bond, leading to the release of the perfume component and of the primary amine compound. This can be achieved by either hydrolysis, photochemical cleavage, oxidative cleavage, or enzymatic cleavage.

**[0118]** For  $\beta$ -aminoketone compounds, treatment with air moisture and/or water successfully releases the perfume component and the primary amine compound. However, other means of release are not excluded like hydrolysis, photochemical cleavage, oxidative cleavage, or enzymatic cleavage.

**[0119]** Still other means of release for imine as well as  $\beta$ -aminoketone compounds can be considered such as by the steaming step of ironing the treated fabric, tumble-drying, and/or wearing.

#### Laundry and cleaning compositions

**[0120]** The present invention include both laundry and cleaning compositions which are typically used for laundering fabrics and cleaning hard surfaces such as dishware, floors, bathrooms, toilet, kitchen and other surfaces in need of a delayed release of perfume ketone and/or aldehyde. Accordingly, by laundry and cleaning compositions, these are to be understood to include not only detergent compositions which provide fabric cleaning benefits, but also compositions such as hard surface cleaning which provide hard surface cleaning benefit.

**[0121]** Preferred are those laundry compositions which result in contacting the compound of the invention with fabric.

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[0122] Preferably, the amine reaction product(s) which is incorporated into such laundry and cleaning compositions provides a dry surface Odor Index of more than 5 preferably at least 10.

[0123] By Dry Surface Odor Index, it is meant that the amine reaction product(s) provides a Delta of more than 5, wherein Delta is the difference between the Odor Index of the dry surface treated with amine reaction product(s) and the Odor Index of the dry surface treated with only the perfume raw material.

### Measurement method of Dry Surface Odor Index:

[0124] For the above Dry Surface Odor Index, the amine reaction product suitable for use in the present invention needs to fulfill at least one of the following two tests. Preferred amine reaction product suitable for use in the present invention fulfill both test.

#### 1)-For fabric surface

##### Product preparation:

[0125] The amine reaction product is added to the unperfumed product base. Levels of amine reaction product are selected so as to obtain an odor grade on the dry fabric of at least 20. After careful mixing, by shaking the container in case of a liquid, with a spatula in case of a powder, the product is allowed to sit for 24 hrs.

##### Washing process:

[0126] The resulting product is added into the washing machine in the dosage and in the dispenser appropriate for its category. The quantity corresponds to recommended dosages made for the corresponding market products: typically between 70 and 150 g for a detergent powder or liquid via current dosing device like granulette, or arielle. The load is composed of four bath towels (170g) using a Miele W830 washing machine at 40°C short cycle, water input : 15°Hardness at a temperature of 10-18°C, and full spin of 1200rpm.

[0127] The same process is applied for the corresponding free perfume ingredient in consideration and is used as the reference. Dosages, fabric loads and washing cycles for the reference and the sample are identical.

##### Drying Process:

[0128] Within two hours after the end of the washing cycle, spinned but still wet fabrics are assessed for their odors using the scale mentioned below. Afterwards, half of the fabric pieces are hung on a line for 24 hr drying, away from any possible contaminations. Unless specified, this drying takes place indoor. Ambient conditions are at temperature between 18-25°C and air moisture between 50-80%. The other half is placed in a tumble drier and undergoes a full "very dry" cycle, i.e. in a Miele, Novotronic T430 set on program white-extra dry (full cycle). Tumble dry fabrics are also assessed on the next day. Fabrics are then stored in opened aluminum bags in an odor free room, and assessed again after 7 days.

##### Odor Evaluations:

[0129] Odor is assessed by expert panellist smelling the fabrics. A 0-100 scale is used for all fabric odor gradings. The grading scale is as follows:

100 = extremely strong perfume odor

75 = very strong perfume odor

50 = strong odor

40 = moderate perfume odor

30 = slight perfume odor

20 = weak perfume odor

10 = very weak perfume odor

0 = no odor

[0130] A difference of more than 5 grades after one day and/or 7 days between the amine reaction product and the perfume raw material is statistically significant. A difference of 10 grades or more after one day and/or 7 days represents a step-change. In other words, when a difference of grade of more than 5, preferably at least 10 is observed between the amine reaction product and the perfume raw material, after either 1 day or 7 days or both 1 day

and 7 days, it can be concluded that the amine reaction product is suitable for use in the present invention, provided that the amine compound fulfill the Odor Intensity Index.

## 2)-For hard surface:

### Product preparation:

[0131] The perfume raw material or blend thereof is added and carefully mixed at 0.255% in the unperfumed Hard Surface Cleaner base. After mixing and standing for 24 hrs, the homogeneity of the product is checked. In case of phase separation due to poor solubility of the perfume ingredient(s) an appropriate amount of Sodium p. Cymene Sulfonate or another solubilising agent is added till a homogeneous solution is obtained.

### Cleaning process:

[0132] Five grams of this solution are evenly applied on the upper side of a ceramic tile (875 square cm, e.g. from Vileroy-Boch). After 1 minute the tile is rinsed with 1 liter of tap water. The tile is then placed in a vertical position for 3 minutes to allow the rinse water to drip off.

[0133] Finally, the tile is placed in a clean and aerated perspex box (38 x 40 x 32 cm) with a removable cover that has a sliding-lid (10 x 10 cm) to allow expert evaluators to smell the interior phase of the box. The odor in the box is evaluated just after placing the tile in it (fresh reading) and after 1, 2 and 6 hours.

### Odor Evaluation:

[0134] The grading scale is as follows:

50 = very strong odor

40 = strong odor

30 = moderate odor

20 = slight odor

10 = weak odor

0 = no odor

[0135] Every test includes a blanc (unperfumed Hard Surface Cleaner) and in the case of testing perfume precursor, so-called amine reaction product the corresponding free perfume ingredient is also included so that the effect of the carrier is adequately measured.

[0136] Again as for the Dry surface Odor Index method for fabrics, a difference of more than 5 grades after 1 day and/or 7 days between the amine reaction product and the perfume raw material is statistically significant. A difference of 10 grades or more after 1 day and/or 7 days represents a step-change. In other words, when a difference of grade of more than 5, preferably at least 10 is observed between the amine reaction product and the perfume raw material, after either 1 day or 7 day or both 1 day and 7 days, it can be concluded that the amine reaction product is suitable for use in the present, provided that the amine compound fulfill the Odor Intensity Index.

[0137] The amine reaction product as defined herein before typically is comprised at from 0.0001% to 10%, preferably from 0.001% to 5%, and more preferably from 0.01% to 2%, by weight of the composition. Mixtures of the compounds may also be used herein.

[0138] Incorporation of the amine reaction product in the laundry and cleaning compositions can conveniently be carried out, if necessary, by conventional incorporation means, such as by spray-on, encapsulation like starch encapsulation, e.g. as described in GB1464616, dry addition, or by encapsulation in cyclodextrin. Preferably, the amine reaction product is preformed before incorporation into the laundry and cleaning compositions. In other words, the perfume component and the amine compound are first reacted together to obtain the resulting amine reaction product as defined in the present invention and only once formed incorporated into the laundry and cleaning compositions. By being preformed before the incorporation in fully formulated composition, a better control of the compound being made is obtained. Hence, the interaction with perfume composition which may be present in fully formulated composition is avoided as well as side reaction that could occur. Further, by such means of incorporation, efficient control of the yield and purity of the compound is obtained.

[0139] Most preferably, when the laundry and cleaning composition comprises a perfume, the amine reaction product is incorporated in the composition separately from the perfume. By this means, the amine reaction product and its subsequent perfume release is more controlled.

[0140] Typically the laundry and cleaning composition comprises a detergent ingredient and further optional ingredients as described hereinafter as optional ingredients.

Deterstive ingredients

**[0141]** Non-limiting examples of surfactants useful herein typically at levels from 1% to 55%, by weight, include the conventional C<sub>11</sub>-C<sub>18</sub> alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C<sub>10</sub>-C<sub>20</sub> alkyl sulfates ("AS"), the C<sub>10</sub>-C<sub>18</sub> secondary (2,3) alkyl sulfates of the formula CH<sub>3</sub>(CH<sub>2</sub>)<sub>x</sub>(CHOSO<sub>3</sub><sup>-</sup> M<sup>+</sup>) CH<sub>3</sub> and CH<sub>3</sub>(CH<sub>2</sub>)<sub>y</sub>(CHOSO<sub>3</sub><sup>-</sup> M<sup>+</sup>) CH<sub>2</sub>CH<sub>3</sub> where x and (y + 1) are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy sulfates ("AE<sub>x</sub>S"; especially x up to 7 EO ethoxy sulfates), C<sub>10</sub>-C<sub>18</sub> alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C<sub>10</sub>-C<sub>18</sub> glycerol ethers, the C<sub>10</sub>-C<sub>18</sub> alkyl polyglycosides and their corresponding sulfated polyglycosides, and C<sub>12</sub>-C<sub>18</sub> alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C<sub>12</sub>-C<sub>18</sub> alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C<sub>6</sub>-C<sub>12</sub> alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C<sub>12</sub>-C<sub>18</sub> betaines and sulfobetaines ("sultaines"), C<sub>10</sub>-C<sub>18</sub> amine oxides, cationic surfactants and the like, can also be included in the overall compositions. The C<sub>10</sub>-C<sub>18</sub> N-alkyl polyhydroxy fatty acid amides can also be used. Typical examples include the C<sub>12</sub>-C<sub>18</sub> N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C<sub>10</sub>-C<sub>18</sub> N-(3-methoxypropyl) glucamide. The N-propyl through N-hexyl C<sub>12</sub>-C<sub>18</sub> glucamides can be used for low sudsing. C<sub>10</sub>-C<sub>20</sub> conventional soaps may also be used. If high sudsing is desired, the branched-chain C<sub>10</sub>-C<sub>16</sub> soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

**[0142]** Fully formulated laundry and cleaning compositions preferably contain, in addition to the hereinbefore described components, one or more of the following ingredients.

Builders

**[0143]** Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

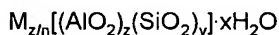
**[0144]** The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least 1% builder, preferably from 1% to 80%. Liquid formulations typically comprise from 5% to 50%, more typically 5% to 30%, by weight, of detergent builder. Granular formulations typically comprise from 1% to 80%, more typically from 5% to 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

**[0145]** Inorganic or P-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the triphosphates, pyrophosphates, and glassy polymeric meta-phosphates), phosphonates, phytic acid, silicates, carbonates (including bicarbonates and sesquicarbonates), sulphates, and aluminosilicates. However, non-phosphate builders are required in some locales. Importantly, the compositions herein function surprisingly well even in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

**[0146]** Examples of silicate builders are the alkali metal silicates, particularly those having a SiO<sub>2</sub>:Na<sub>2</sub>O ratio in the range 1.0:1 to 3.2:1 and layered silicates, such as the layered sodium silicates described in U.S. 4,664,839. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta-Na<sub>2</sub>SiO<sub>5</sub> morphology form of layered silicate. It can be prepared by methods such as those described in DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula NaMSi<sub>x</sub>O<sub>2x+1</sub>·yH<sub>2</sub>O wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta-Na<sub>2</sub>SiO<sub>5</sub> (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilizing agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in DE 2,321,001.

**[0147]** Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:

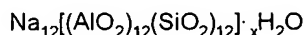


wherein z and y are integers usually of at least 6, the molar ratio of z to y is in the range from 1.0 to 0, and x is an integer from 0 to 264, and M is a Group IA or IIA element, e.g., Na, K, Mg, Ca with valence n.

**[0148]** Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. 3,985,669. Preferred synthetic crystalline

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aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from 20 to 30, especially 27. This material is known as Zeolite A. Dehydrated zeolites (x = 0 - 10) may also be used herein. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

[0149] Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralized salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

[0150] Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in Berg, U.S. 3,128,287, U.S. 3,635,830. See also "TMS/TDS" builders of U.S. 4,663,071. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

[0151] Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, pyromellitic, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

[0152] Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

[0153] Also suitable in the detergent compositions of the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. 4,566,984. Useful succinic acid builders include the C<sub>5</sub>-C<sub>20</sub> alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in EP 0,200,263.

[0154] Other suitable polycarboxylates are disclosed in U.S. 4,144,226 and in U.S. 3,308,067. See also U.S. 3,723,322.

[0155] Fatty acids, e.g., C<sub>12</sub>-C<sub>18</sub> monocarboxylic acids such as oleic acid and/or its salts, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

[0156] In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundering operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1, 1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

### Bleaching Compounds - Bleaching Agents and Bleach Activators

[0157] The detergent compositions herein may optionally contain bleaching agents or bleaching compositions containing a bleaching agent and one or more bleach activators. When present, bleaching agents will typically be at levels of from 1% to 30%, more typically from 5% to 20%, of the detergent composition, especially for fabric laundering. If present, the amount of bleach activators will typically be from 0.1% to 60%, more typically from 0.5% to 40% of the bleaching composition comprising the bleaching agent-plus-bleach activator.

[0158] The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile cleaning or other cleaning purposes that are now known or become known. These include oxygen bleaches as well as other bleaching agents like hypochlorite bleaching agents. Perborate bleaches, e.g., sodium perborate (e.g., mono- or tetra-hydrate) can be used herein. When hypochlorite is used, a highly preferred hypochlorite bleaching component is an alkali metal hypochlorite. Although alkali metal hypochlorites are preferred, other hypochlorite compounds may also be used herein and can be selected from calcium and magnesium hypochlorite. A preferred alkali metal hypochlorite for use herein is sodium hypochlorite.

[0159] Another category of bleaching agent that can be used without restriction encompasses percarboxylic acid bleaching agents and salts thereof. Suitable examples of this class of agents include magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. 4,483,781, U.S.

740,446, EP 0,133,354, and U.S. 4,412,934. Highly preferred bleaching agents also include 6-nonylamino-6-oxoperoxyacaproic acid as described in U.S. 4,634,551.

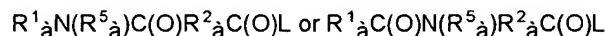
[0160] Peroxygen bleaching agents can also be used. Suitable peroxygen bleaching compounds include sodium carbonate peroxyhydrate and equivalent "percarbonate" bleaches, sodium pyrophosphate peroxyhydrate, urea peroxyhydrate, and sodium peroxide. Persulfate bleach (e.g., OXONE, manufactured commercially by DuPont) can also be used.

[0161] A preferred percarbonate bleach comprises dry particles having an average particle size in the range from 500 micrometers to 1,000 micrometers, not more than 10% by weight of said particles being smaller than 200 micrometers and not more than 10% by weight of said particles being larger than 1,250 micrometers. Optionally, the percarbonate can be coated with silicate, borate or water-soluble surfactants. Percarbonate is available from various commercial sources such as FMC, Solvay and Tokai Denka.

[0162] Mixtures of bleaching agents can also be used.

[0163] Peroxygen bleaching agents, the perborates, the percarbonates, etc., are preferably combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator. Various non-limiting examples of activators are disclosed in U.S. 4,915,854, and U.S. 4,412,934. The nonanoyloxybenzene sulfonate (NOBS), 3,5,5-trimethyl hexanoyl oxybenzene sulfonate (ISONOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used. See also U.S. 4,634,551 for other typical bleaches and activators useful herein.

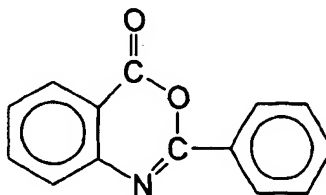
Highly preferred amido-derived bleach activators are those of the formulae:



wherein  $R^1_a$  is an alkyl group containing from 6 to 12 carbon atoms,  $R^2_a$  is an alkylene containing from 1 to 6 carbon atoms,  $R^5_a$  is H or alkyl, aryl, or alkaryl containing from 1 to 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

[0164] Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzene sulfonate, (6-decanamido-caproyl)oxybenzenesulfonate, and mixtures thereof as described in U.S. Patent 4,634,551, incorporated herein by reference.

[0165] Another class of bleach activators comprises the benzoxazin-type activators disclosed by Hodge et al in U.S. Patent 4,966,723. A highly preferred activator of the benzoxazin-type is:



[0166] Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:



wherein  $R^6_a$  is H or an alkyl, aryl, alkoxyaryl, or alkaryl group containing from 1 to 12 carbon atoms. Highly preferred lactam activators include benzoyl caprolactam, octanoyl caprolactam, 3,5,5-trimethylhexanoyl caprolactam, nonanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, benzoyl valerolactam, octanoyl valerolactam, decanoyl valerolactam, undecenoyl valerolactam, nonanoyl valerolactam, 3,5,5-trimethylhexanoyl valerolactam and mixtures thereof. See also U.S. Patent 4,545,784, issued to Sanderson, October 8, 1985, incorporated herein by reference, which discloses acyl caprolactams, including benzoyl caprolactam, adsorbed into sodium perborate.

[0167] Bleaching agents other than oxygen bleaching agents are also known in the art and can be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the



sulfonated zinc and/or aluminum phthalocyanines. See U.S. 4,033,718. If used, detergent compositions will typically contain from 0.025% to 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

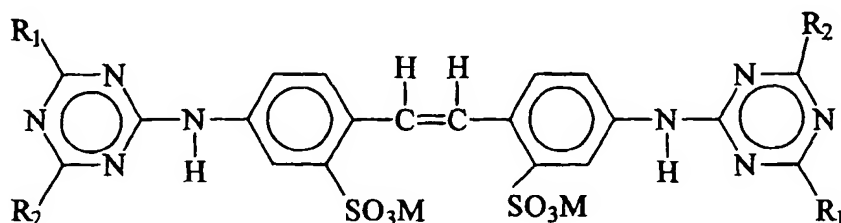
[0168] If desired, the bleaching compounds can be catalyzed by means of a manganese compound. Such compounds are well-known in the art and include, for example, the manganese-based catalysts disclosed in U.S. 5,246,621, U.S. 5,244,594; U.S. 5,194,416; U.S. 5,114,606; and EP 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include  $\text{Mn}^{\text{IV}}_{\text{a}_2}(\text{u-O})_3(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{PF}_6)_2$ ,  $\text{Mn}^{\text{III}}_{\text{a}}12(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_2$ ,  $\text{Mn}^{\text{IV}}_{\text{a}_4}(\text{u-O})_6(1,4,7\text{-triacyclononane})_4(\text{ClO}_4)_4$ ,  $\text{Mn}^{\text{III}}_{\text{a}}\text{Mn}^{\text{IV}}_{\text{a}_4}(\text{u-O})_1(\text{u-OAc})_2(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})_2(\text{ClO}_4)_3$ ,  $\text{Mn}^{\text{IV}}_{\text{a}}(1,4,7\text{-trimethyl-1,4,7-triazacyclononane})-(\text{OCH}_3)_3(\text{PF}_6)$ , and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following US Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

[0169] As a practical matter, and not by way of limitation, the compositions and processes herein can be adjusted to provide on the order of at least one part per ten million of the active bleach catalyst species in the aqueous washing liquor, and will preferably provide from 0.1 ppm to 700 ppm, more preferably from 1 ppm to 500 ppm, of the catalyst species in the laundry liquor.

### Brighteners

[0170] The compositions herein can also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from 0.001% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein  $R_1$  is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl;  $R_2$  is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula,  $R_1$  is anilino,  $R_2$  is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX® by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the rinse added compositions herein.

When in the above formula,  $R_1$  is anilino,  $R_2$  is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX® by Ciba-Geigy Corporation.

When in the above formula,  $R_1$  is anilino,  $R_2$  is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX® by Ciba Geigy Corporation.

### Soil Release Agent

[0171] In the present invention, an optional soil release agent can be added. Typical levels of incorporation in the composition are from 0% to 10%, preferably from 0.2% to 5%, of a soil release agent. Preferably, such a soil release agent is a polymer.

[0172] Soil Release agents are desirably used in fabric softening compositions of the instant invention. Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions of this invention. Polymeric soil release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

[0173] If utilized, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

[0174] The following, all included herein by reference, describe soil release polymers suitable for use in the present invention. U.S. 3,959,230 Hays, issued May 25, 1976; U.S. 3,893,929 Basadur, issued July 8, 1975; U.S. 4,000,093, Nicol, *et al.*, issued December 28, 1976; U.S. Patent 4,702,857 Gosselink, issued October 27, 1987; U.S. 4,968,451, Scheibel *et al.*, issued November 6, 1987; U.S. 4,702,857, Gosselink, issued October 27, 1987; U.S. 4,711,730, Gosselink *et al.*, issued December 8, 1987; U.S. 4,721,580, Gosselink, issued January 26, 1988; U.S. 4,877,896, Maldonado *et al.*, issued October 31, 1989; U.S. 4,956,447, Gosselink *et al.*, issued September 11, 1990; U.S. 5,415,807 Gosselink *et al.*, issued May 16, 1995; European Patent Application 0 219 048, published April 22, 1987 by Kud, *et al.*

[0175] Further suitable soil release agents are described in U.S. 4,201,824, Violland *et al.*; U.S. 4,240,918 Lagasse *et al.*; U.S. 4,525,524 Tung *et al.*; U.S. 4,579,681, Ruppert *et al.*; U.S. 4,240,915; U.S. 4,787,989; U.S. 4,525,524; EP 279,134 A, 1988, to Rhone-Poulenc Chemie; EP 457,205 A to BASF (1991); and DE 2,335,044 to Unilever N. V., 1974 all incorporated herein by reference.

[0176] Commercially available soil release agents include the METOLOSE SM100, METOLOSE SM200 manufactured by Shin-etsu Kagaku Kogyo K.K., SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (Germany), ZELCON 5126 (from Dupont) and MILEASE T (from ICI).

#### Scum Dispersant

[0177] In the present invention, the premix can be combined with an optional scum dispersant, other than the soil release agent, and heated to a temperature at or above the melting point(s) of the components.

The preferred scum dispersants herein are formed by highly ethoxylating hydrophobic materials. The hydrophobic material can be a fatty alcohol, fatty acid, fatty amine, fatty acid amide, amine oxide, quaternary ammonium compound, or the hydrophobic moieties used to form soil release polymers. The preferred scum dispersants are highly ethoxylated, e.g., more than 17, preferably more than 25, more preferably more than 40, moles of ethylene oxide per molecule on the average, with the polyethylene oxide portion being from 76% to 97%, preferably from 81% to 94%, of the total molecular weight.

The level of scum dispersant is sufficient to keep the scum at an acceptable, preferably unnoticeable to the consumer, level under the conditions of use, but not enough to adversely affect softening. For some purposes it is desirable that the scum is nonexistent. Depending on the amount of anionic or nonionic detergent, etc., used in the wash cycle of a typical laundering process, the efficiency of the rinsing steps prior to the introduction of the compositions herein, and the water hardness, the amount of anionic or nonionic detergent surfactant and detergency builder (especially phosphates and zeolites) entrapped in the fabric (laundry) will vary. Normally, the minimum amount of scum dispersant should be used to avoid adversely affecting softening properties. Typically scum dispersion requires at least 2%, preferably at least 4% (at least 6% and preferably at least 10% for maximum scum avoidance) based upon the level of softener active. However, at levels of 10% (relative to the softener material) or more, one risks loss of softening efficacy of the product especially when the fabrics contain high proportions of nonionic surfactant which has been absorbed during the washing operation.

Preferred scum dispersants are: Brij 700®; Varonic U-250®; Genapol T-500®, Genapol T-800®; Plurafac A-79®, and Neodol 25-50®.

#### Bactericides

[0178] Examples of bactericides used in the compositions of this invention include glutaraldehyde, formaldehyde, 2-bromo-2-nitro-propane-1,3-diol sold by Inolex Chemicals, located in Philadelphia, Pennsylvania, under the trade name Bronopol®, and a mixture of 5-chloro-2-methyl-4-isothiazoline-3-one and 2-methyl-4-isothiazoline-3-one sold by Rohm and Haas Company under the trade name Kathon 1 to 1,000 ppm by weight of the agent.

#### Perfume

[0179] The present invention can contain any detergent compatible perfume. Suitable perfumes are disclosed in U.S. Pat. 5,500,138, said patent being incorporated herein by reference.

As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced) odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

[0180] Examples of perfume ingredients useful in the perfumes of the present invention compositions include, but are not limited to, hexyl cinnamic aldehyde; amyl cinnamic aldehyde; amyl salicylate; hexyl salicylate; terpeneol; 3,7-dimethyl-*cis*-2,6-octadien-1-ol; 2,6-dimethyl-2-octanol; 2,6-dimethyl-7-octen-2-ol; 3,7-dimethyl-3-octanol; 3,7-dimethyl-*trans*-2,6-octadien-1-ol; 3,7-dimethyl-6-octen-1-ol; 3,7-dimethyl-1-octanol; 2-methyl-3-(para-*tert*-butylphenyl)-propionaldehyde; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde; tricyclodecanyl propionate; tricyclodecanyl acetate; anisaldehyde; 2-methyl-2-(para-*iso*-propylphenyl)-propionaldehyde; ethyl-3-methyl-3-phenylglycidate; 4-(para-hydroxyphenyl)-butan-2-one; 1-(2,6,6-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; para-

methoxyacetophenone; para-methoxy-alpha-phenylpropene; methyl-2-n-hexyl-3-oxo-cyclopentane carboxylate; undecalactone gamma.

Additional examples of fragrance materials include, but are not limited to, orange oil; lemon oil; grapefruit oil; bergamot oil; clove oil; dodecalactone gamma; methyl-2-(2-pentyl-3-oxo-cyclopentyl) acetate; beta-naphthol methylether; methyl-beta-naphthylketone; coumarin; decylaldehyde; benzaldehyde; 4-tert-butylcyclohexyl acetate; alpha,alpha-dimethylphenethyl acetate; methylphenylcarbinyl acetate; Schiff's base of 4-(4-hydroxy-4-methylpentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate; cyclic ethyleneglycol diester of tridecandioic acid; 3,7-dimethyl-2,6-octadiene-1-nitrile; ionone gamma methyl; ionone alpha; ionone beta; petitgrain; methyl cedrylone; 7-acetyl-1,2,3,4,5,6,7,8-octahydro-1,1,6,7-tetramethyl-naphthalene; ionone methyl; methyl-1,6,10-trimethyl-2,5,9-cyclododecatrien-1-yl ketone; 7-acetyl-1,1,3,4,4,6-hexamethyl tetralin; 4-acetyl-6-tert-butyl-1,1-dimethyl indane; benzophenone; 6-acetyl-1,1,2,3,3,5-hexamethyl indane; 5-acetyl-3-isopropyl-1,1,2,6-tetramethyl indane; 1-dodecanal; 7-hydroxy-3,7-dimethyl octanal; 10-undecen-1-al; iso-hexenyl cyclohexyl carboxaldehyde; formyl tricyclodecan; cyclopentadecanolid; 16-hydroxy-9-hexadecenoic acid lactone; 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-gamma-2-benzopyrane; ambroxane; dodecahydro-3a,6,6,9a-tetramethylnaphtho-[2,1b]furan; cedrol; 5-(2,2,3-trimethylcyclopent-3-enyl)-3-methylpentan-2-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopenten-1-yl)-2-buten-1-ol; caryophyllene alcohol; cedryl acetate; para-tert-butylcyclohexyl acetate; patchouli; olibanum resinoid; labdanum; vetiver; copaiba balsam; fir balsam; and condensation products of: hydroxycitronellal and methyl anthranilate; hydroxycitronellal and indol; phenyl acetaldehyde and indol; 4-(4-hydroxy-4-methyl pentyl)-3-cyclohexene-1-carboxaldehyde and methyl anthranilate.

More examples of perfume components are geraniol; geranyl acetate; linalool; linalyl acetate; tetrahydrolinalool; citronellol; citronellyl acetate; dihydromyrcenol; dihydromyrcenyl acetate; tetrahydromyrcenol; terpinyl acetate; nopol; nopol acetate; 2-phenylethanol; 2-phenylethyl acetate; benzyl alcohol; benzyl acetate; benzyl salicylate; benzyl benzoate; styrallyl acetate; dimethylbenzylcarbinol; trichloromethylphenylcarbinyl methylphenylcarbinyl acetate; isononyl acetate; vetiveryl acetate; vetiverol; 2-methyl-3-(p-tert-butylphenyl)-propanal; 2-methyl-3-(p-isopropylphenyl)-propanal; 3-(p-tert-butylphenyl)-propanal; 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde; 4-acetoxy-3-pentyltetrahydropyran; methyl dihydrojasmonate; 2-n-heptylcyclopentanone; 3-methyl-2-pentyl-cyclopentanone; n-decanal; n-dodecanal; 9-decenol-1; phenoxyethyl isobutyrate; phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethylacetal; geranonitrile; citronellonitrile; cedryl acetal; 3-isocamphylcyclohexanol; cedryl methylether; isolongifolanone; aubepine nitrile; aubepine; heliotropine; eugenol; vanillin; diphenyl oxide; hydroxycitronellal ionones; methyl ionones; isomethyl ionones; irones; cis-3-hexenol and esters thereof; indane musk fragrances; tetralin musk fragrances; isochroman musk fragrances; macrocyclic ketones; macrolactone musk fragrances; ethylene brassylate.

The perfumes useful in the present invention compositions are substantially free of halogenated materials and nitromusks.

Suitable solvents, diluents or carriers for perfumes ingredients mentioned above are for examples, ethanol, isopropanol, diethylene glycol, monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, etc. The amount of such solvents, diluents or carriers incorporated in the perfumes is preferably kept to the minimum needed to provide a homogeneous perfume solution.

**[0181]** Perfume can be present at a level of from 0% to 10%, preferably from 0.1 % to 5%, and more preferably from 0.2% to 3%, by weight of the finished composition. Fabric softener compositions of the present invention provide improved fabric perfume deposition.

#### Chelating Agents

**[0182]** The compositions and processes herein can optionally employ one or more copper and/or nickel chelating agents ("chelators"). Such water-soluble chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures thereof, all as hereinafter defined. The whiteness and/or brightness of fabrics are substantially improved or restored by such chelating agents and the stability of the materials in the compositions are improved. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

**[0183]** Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetra-amine-hexacetates, diethylenetriaminepentaacetates, and ethanoldiglycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

**[0184]** Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) as DEQUEST. Preferred, these amino phosphonates do not contain alkyl or alkenyl groups with more than about 6 carbon atoms.

**[0185]** Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

**[0186]** A preferred biodegradable chelator for use herein is ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, November 3, 1987, to Hartman and Perkins.

**[0187]** The compositions herein may also contain water-soluble methyl glycine diacetic acid (MGDA) salts (or acid form) as a chelant or co-builder useful with, for example, insoluble builders such as zeolites, layered silicates and

the like.

[0188] Preferred chelating agents include DETMP, DETPA, NTA, EDDS and mixtures thereof.

[0189] If utilized, these chelating agents will generally comprise from about 0.1% to about 15% by weight of the fabric care compositions herein. More preferably, if utilized, the chelating agents will comprise from about 0.1% to about 3.0% by weight of such compositions.

#### Crystal growth inhibitor component

[0190] The compositions of the present invention can further contain a crystal growth inhibitor component, preferably an organodiphosphonic acid component, incorporated preferably at a level of from 0.01% to 5%, more preferably from 0.1% to 2% by weight of the compositions.

[0191] By organo diphosphonic acid it is meant herein an organo diphosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrant components.

[0192] The organo diphosphonic acid is preferably a C<sub>1</sub>-C<sub>4</sub> diphosphonic acid, more preferably a C<sub>2</sub> diphosphonic acid, such as ethylene diphosphonic acid, or most preferably ethane 1-hydroxy-1,1-diphosphonic acid (HEDP) and may be present in partially or fully ionized form, particularly as a salt or complex.

[0193] Still useful herein as crystal growth inhibitor are the organic monophosphonic acids.

Organo monophosphonic acid or one of its salts or complexes is also suitable for use herein as a CGI.

[0194] By organo monophosphonic acid it is meant herein an organo monophosphonic acid which does not contain nitrogen as part of its chemical structure. This definition therefore excludes the organo aminophosphonates, which however may be included in compositions of the invention as heavy metal ion sequestrants.

[0195] The organo monophosphonic acid component may be present in its acid form or in the form of one of its salts or complexes with a suitable counter cation. Preferably any salts/complexes are water soluble, with the alkali metal and alkaline earth metal salts/complexes being especially preferred.

[0196] A preferred organo monophosphonic acid is 2-phosphonobutane-1,2,4-tricarboxylic acid commercially available from Bayer under the tradename of Bayhibit.

#### Enzyme

[0197] The compositions and processes herein can optionally employ one or more enzymes such as lipases, proteases, cellulase, amylases and peroxidases. A preferred enzyme for use herein is a cellulase enzyme. Indeed, this type of enzyme will further provide a color care benefit to the treated fabric. Cellulases usable herein include both bacterial and fungal types, preferably having a pH optimum between 5 and 9.5. U.S. 4,435,307 discloses suitable fungal cellulases from *Humicola insolens* or *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk, *Dolabella Auricula Solander*. Suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. CAREZYME® and CELLUZYME® (Novo) are especially useful. Other suitable cellulases are also disclosed in WO 91/17243 to Novo, WO 96/34092, WO 96/34945 and EP-A-0,739,982. In practical terms for current commercial preparations, typical amounts are up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the detergent composition. Stated otherwise, the compositions herein will typically comprise from 0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation. In the particular cases where activity of the enzyme preparation can be defined otherwise such as with cellulases, corresponding activity units are preferred (e.g. CEVU or cellulase Equivalent Viscosity Units). For instance, the compositions of the present invention can contain cellulase enzymes at a level equivalent to an activity from 0.5 to 1000 CEVU/gram of composition. Cellulase enzyme preparations used for the purpose of formulating the compositions of this invention typically have an activity comprised between 1,000 and 10,000 CEVU/gram in liquid form, around 1,000 CEVU/gram in solid form.

[0198] Other preferred optional ingredients include enzyme stabilisers, polymeric soil release agents, materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process (i.e., dye transfer inhibiting agents), polymeric dispersing agents, suds suppressors, optical brighteners or other brightening or whitening agents, chelating agents, fabric softening clay, anti-static agents, other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for liquid formulations and solid fillers for bar compositions.

[0199] Liquid detergent compositions can contain water and other solvents as carriers. Low molecular weight primary or secondary alcohols exemplified by methanol, ethanol, propanol, and isopropanol are suitable. Monohydric alcohols are preferred for solubilizing surfactant, but polyols such as those containing from 2 to 6 carbon atoms and from 2 to 6 hydroxy groups (e.g., 1,3-propanediol, ethylene glycol, glycerine, and 1,2-propanediol) can also be used. The compositions may contain from 5% to 90%, typically 10% to 50% of such carriers.

[0200] Granular detergents can be prepared, for example, by spray-drying (final product density 520 g/l) or agglomerating (final product density above 600 g/l) the Base Granule. The remaining dry ingredients can then be admixed in granular or powder form with the Base Granule, for example in a rotary mixing drum, and the liquid ingredients (e.g., nonionic surfactant and perfume) can be sprayed on.

[0201] The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between 6.5 and 11, preferably between 7.5 and 10.5. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage levels include the use of buffers, alkalis, acids, etc., and are well-known to those skilled in the art.

Method of use

**[0202]** Also provided herein is a method for providing a delayed release of an active ketone or aldehyde which comprises the step of contacting the surface to be treated with a compound or composition of the invention, and thereafter contacting the treated surface with a material, preferably an aqueous medium like moisture or any other means susceptible of releasing the perfume from the amine reaction product.

**[0203]** By "surface", it is meant any surface onto which the compound can deposit. Typical examples of such material are fabrics, hard surfaces such as dishware, floors, bathrooms, toilet, kitchen and other surfaces in need of a delayed release of a perfume ketone and/or aldehyde such as that with litter like animal litter. Preferably, the surface is selected from a fabric, a tile, a ceramic; more preferably is a fabric.

**[0204]** By "delayed release" is meant release of the active component (e.g perfume) over a longer period of time than by the use of the active (e.g., perfume) itself.

Abbreviations used in the following laundry and cleaning composition Examples

**[0205]** In the laundry and cleaning compositions, the abbreviated component identifications have the following meanings:

**[0206]** In the detergent compositions, the abbreviated component identifications have the following meanings:

LAS	: Sodium linear C <sub>11-13</sub> alkyl benzene sulfonate
TAS	: Sodium tallow alkyl sulfate
CxyAS	: Sodium C <sub>1x</sub> - C <sub>1y</sub> alkyl sulfate
C46SAS	: Sodium C <sub>14</sub> - C <sub>16</sub> secondary (2,3) alkyl sulfate
CxyEzS	: Sodium C <sub>1x</sub> - C <sub>1y</sub> alkyl sulfate condensed with z moles of ethylene oxide
CxyEz	: C <sub>1x</sub> - C <sub>1y</sub> predominantly linear primary alcohol condensed with an average of z moles of ethylene oxide
QAS	: R <sub>2</sub> .N <sup>+</sup> â (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>12</sub> - C <sub>14</sub>
QAS 1	: R <sub>2</sub> .N <sup>+</sup> â (CH <sub>3</sub> ) <sub>2</sub> (C <sub>2</sub> H <sub>4</sub> OH) with R <sub>2</sub> = C <sub>8</sub> - C <sub>11</sub>
APA	: C <sub>8</sub> - C <sub>10</sub> amido propyl dimethyl amine
Soap	: Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut fatty acids
STS	: Sodium toluene sulphonate
CFAA	: C <sub>12</sub> - C <sub>14</sub> (coco) alkyl N-methyl glucamide
TFAA	: C <sub>16</sub> - C <sub>18</sub> alkyl N-methyl glucamide
TPKFA	: C <sub>12</sub> - C <sub>14</sub> topped whole cut fatty acids
STPP	: Anhydrous sodium tripolyphosphate
TSPP	: Tetrasodium pyrophosphate
Zeolite A	: Hydrated sodium aluminosilicate of formula Na <sub>12</sub> (AlO <sub>2</sub> SiO <sub>2</sub> ) <sub>12</sub> .27H <sub>2</sub> O having a primary particle size in the range from 0.1 to 10 micrometers (weight expressed on an anhydrous basis)
NaSKS-6	: Crystalline layered silicate of formula δ- Na <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>
Citric acid	: Anhydrous citric acid
Borate	: Sodium borate
Carbonate	: Anhydrous sodium carbonate with a particle size between 200µm and 900µm
Bicarbonate	: Anhydrous sodium bicarbonate with a particle size distribution between 400µm and 1200µm
Silicate	: Amorphous sodium silicate (SiO <sub>2</sub> :Na <sub>2</sub> O = 2.0:1)
Sulfate	: Anhydrous sodium sulfate
Mg sulfate	: Anhydrous magnesium sulfate
Citrate	: Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and 850µm
MA/AA	: Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
MA/AA (1)	: Copolymer of 4:6 maleic/acrylic acid, average molecular weight about 10,000
AA	: Sodium polyacrylate polymer of average molecular weight 4,500
CMC	: Sodium carboxymethyl cellulose
Cellulose ether	: Methyl cellulose ether with a degree of polymerization of 650 available from Shin Etsu Chemicals
Protease	: Proteolytic enzyme, having 3.3% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Savinase
Protease I	: Proteolytic enzyme, having 4% by weight of active enzyme, as described in WO 95/10591, sold by Genencor Int. Inc.
Alcalase	: Proteolytic enzyme, having 5.3% by weight of active enzyme, sold by NOVO Industries A/S
Cellulase	: Cellulytic enzyme, having 0.23% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Carezyme
Amylase	: Amylolytic enzyme, having 1.6% by weight of active enzyme, sold by NOVO Industries A/S

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		under the tradename Termamyl 120T
	Lipase	: Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase
	Lipase (1)	: Lipolytic enzyme, having 2.0% by weight of active enzyme, sold by NOVO Industries A/S under the tradename Lipolase Ultra
5	Endolase	: Endoglucanase enzyme, having 1.5% by weight of active enzyme, sold by NOVO Industries A/S
	PB4	: Sodium perborate tetrahydrate of nominal formula $\text{NaBO}_2 \cdot 3\text{H}_2\text{O} \cdot \text{H}_2\text{O}_2$
	PB1	: Anhydrous sodium perborate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$
	Percarbonate	: Sodium percarbonate of nominal formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$
	NOBS	: Nonanoyloxybenzene sulfonate in the form of the sodium salt
10	NAC-OBS	: (6-nonamidocaproyl) oxybenzene sulfonate
	TAED	: Tetraacetylenethylenediamine
	DTPA	: Diethylene triamine pentaacetic acid
	DTPMP	: Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Tradename Dequest 2060
	EDDS	: Ethylenediamine-N,N'-disuccinic acid, (S,S) isomer in the form of its sodium salt.
15	Photoactivated bleach (1)	: Sulfonated zinc phthlocyanine encapsulated in dextrin soluble polymer
	Photoactivated bleach (2)	: Sulfonated aluminophthlocyanine encapsulated in dextrin soluble polymer
	Brightener 1	: Disodium 4,4'-bis(2-sulphostyryl)biphenyl
	Brightener 2	: Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2,2'-disulfonate
	HEDP	: 1,1-hydroxyethane diphosphonic acid
20	PEGx	: Polyethylene glycol, with a molecular weight of x (typically 4,000)
	PEO	: Polyethylene oxide, with an average molecular weight of 50,000
	TEPAE	: Tetraethylenepentaamine ethoxylate
	PVI	: Polyvinyl imidosole, with an average molecular weight of 20,000
	PVP	: Polyvinylpyrrolidone polymer, with an average molecular weight of 60,000
	PVNO	: Polyvinylpyridine N-oxide polymer, with an average molecular weight of 50,000
25	PVPVI	: Copolymer of polyvinylpyrrolidone and vinylimidazole, with an average molecular weight of 20,000
	QEA	: $\text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O})_n)(\text{CH}_3) - \text{N}^+ - \text{C}_6\text{H}_{12} - \text{N}^+ - (\text{CH}_3) \text{bis}((\text{C}_2\text{H}_5\text{O})(\text{C}_2\text{H}_4\text{O}))_n$ , wherein n = from 20 to 30
	SRP 1	: Anionically end capped poly esters
	SRP 2	: Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
30	PEI	: Polyethyleneimine with an average molecular weight of 1800 and an average ethoxylation degree of 7 ethyleneoxy residues per nitrogen
	Silicone antifoam	: Polydimethylsiloxane foam controller with siloxane-oxyalkylene copolymer as dispersing agent with a ratio of said foam controller to said dispersing agent of 10:1 to 100:1
	Opacifier	: Water based monostyrene latex mixture, sold by BASF Aktiengesellschaft under the tradename Lytron 621
35	Wax	: Paraffin wax
	PA30	: Polyacrylic acid of average molecular weight of between about 4,500 - 8,000.
	480N	: Random copolymer of 7:3 acrylate/methacrylate, average molecular weight about 3,500.
	Polygel/carbopol	: High molecular weight crosslinked polyacrylates.
	Metasilicate	: Sodium metasilicate ( $\text{SiO}_2 : \text{Na}_2\text{O}$ ratio = 1.0).
40	Nonionic	: $\text{C}_{13} - \text{C}_{15}$ mixed ethoxylated/propoxylated fatty alcohol with an average degree of ethoxylation of 3.8 and an average degree of propoxylation of 4.5.
	Neodol 45-13	: C14-C15 linear primary alcohol ethoxylate, sold by Shell Chemical CO.
	MnTACN	: Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane.
	PAAC	: Pentaamine acetate cobalt(III) salt.
	Paraffin	: Paraffin oil sold under the tradename Winog 70 by Wintershall.
45	NaBz	: Sodium benzoate.
	BzP	: Benzoyl Peroxide.
	SCS	: Sodium cumene sulphonate.
	BTA	: Benzotriazole.
	pH	: Measured as a 1% solution in distilled water at 20°C.
	ARP1	: Amine reaction product of ethyl 4-aminobenzoate with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde as made from Synthesis example I
50	ARP2	: Amine reaction product of Lupasol P with $\alpha$ -Damascone as made from Synthesis example III
	ARP3	: Amine reaction product of D-glucamine with Citronellal as made from Synthesis example II
	ARP4	: Amine reaction product of tyrosine ethylate with $\alpha$ -Damascone as made from Synthesis example IV method b
55	ARP5	: Amine reaction product of tyrosine ethylate with Hexyl Cinnamic Aldehyde made according to Synthesis example IV method b

[0207] The following are synthesis examples of compounds as defined in the present invention:

#### I-Synthesis of ethyl 4-aminobenzoate with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde

[0208] To an ice cooled stirred solution of 10 g of 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde (0.07 mol) in 35 mL EtOH and molecular sieves (4Å, 20 g) 1eq of the amine was added via an addition funnel. The reaction mixture was stirred under nitrogen atmosphere and protected from light. After 6 days the mixture was filtrated and the solvent was removed. The yield of imine formation is about 90%.

[0209] Similar results were obtained where the 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde was replaced by bourgeonal, or trans-2-nonenal.

#### II-Synthesis of D-glucamine with 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde

[0210] To an ice cooled solution of 1 mmol D-glucamine in about 30 mL EtOH and molecular sieves (4Å, 5 g) 1eq of the 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde was added. The reaction was stirred under nitrogen atmosphere and protected from light. After 3 to 4 days, the molecular sieves and the solvent were removed by filtration and evaporation respectively. The solid imine was obtained in 85 to 90% yield.

[0211] Similar results were obtained where the 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde was replaced by citronellal, trans-2-nonenal, or decanal.

#### III-Synthesis of Lupasol with Damascone

[0212] The  $\beta$ -amino ketone from Lupasol G100 (commercial available by BASF content 50 % water, 50 % Lupasol G100 (Mw. 5000)) and  $\alpha$ -Damascone was prepared using any one of these three different procedures described as follows:

1. Commercially available Lupasol G100 was dried using the following procedure: 20 g of the Lupasol solution was dried at the rotating evaporator during several hours. The obtained residue, still containing about 4.5 g of H<sub>2</sub>O, was azeotropically distilled at the rotating evaporator using toluene. The residue was then placed in the desiccator dried at 60 °C (using P<sub>2</sub>O<sub>5</sub> as water absorbing material). On basis of the obtained weight we concluded that the oil contained less then 10 % H<sub>2</sub>O. On basis of the NMR-spectra we concluded that this is probably less then 5 %. This dried sample was then used in the preparation of  $\beta$ -amino ketones.

1.38 g of the dried Lupasol G100 obtained above was dissolved in 7 mL ethanol. The solution was stirred gently with a magnetic stirrer during a few minutes before 2 g Na<sub>2</sub>SO<sub>4</sub> (anhydrous) was added. After stirring again for a few minutes 2.21 g  $\alpha$ -Damascone was added over a period of 1 minute. After two days reaction, the mixture was filtrated over a Celite filter (vide supra), and the residue washed thoroughly with ethanol. About 180 mL of a light-foaming filtrate was obtained. This was concentrated until dryness using a rotating evaporator and dried over P<sub>2</sub>O<sub>5</sub> in a desiccator at room temperature. About 3.5 g of a colorless oil was obtained.

2. 4.3 g Lupasol G100 solution was (without drying) dissolved in 10 mL ethanol. The solution was stirred with a magnetic stirrer during a few minutes before 3.47 g  $\alpha$ -Damascone was added over a 1.5 minutes period. After two days reaction at room temperature the reaction mixture was filtrated over Celite (vide supra) and the residue washed thoroughly with ethanol. The filtrate (200 mL, light foaming) was concentrated at the evaporator and dried in a desiccator (P<sub>2</sub>O<sub>5</sub> as drying agent) at room temperature. About 5.9 g of a colorless oil was obtained.

3. To 3.0 g of Lupasol G100 solution (used as such) was added 2.41 g  $\alpha$ -Damascone. The mixture was stirred without using solvent. After stirring for 4 days the obtained oil was dissolved in 100 mL THF, dried with MgSO<sub>4</sub>, filtrated and the filtrate concentrated at the rotating evaporator. After drying in the desiccator (P<sub>2</sub>O<sub>5</sub>) at room temperature, about 4.1 g of a colorless oil was obtained. This oil still contained about 13 % (w/w) of THF, even after a prolonged drying (3 days).

[0213] The product obtained from the three procedures had identical NMR-spectra.

[0214] Still another possible route of synthesis is by using Lupasol P. The  $\beta$ -amino ketone from Lupasol P and  $\alpha$ -Damascone was prepared using the procedure described as follows:

[0215] 1.8g Lupasol P solution (50 % H<sub>2</sub>O, 50 % Lupasol Mw. 750000, as obtained from BASF) was dissolved in 7 mL ethanol, the solution was stirred for a few minutes with a magnetic stirrer before 1.44 g  $\alpha$ -Damascone was added. After three days the reaction mixture was filtrated over a celite filter (vide supra) and the residue washed thoroughly with ethanol. After concentrating of the filtrate and drying of the obtained oil in the desiccator (P<sub>2</sub>O<sub>5</sub>) at room temperature, about 3 g of the reaction product between Lupasol and  $\alpha$ -Damascone was obtained.

#### IV- Synthesis of L-Tyrosine ethylate and Damascone

[0216] The amine reaction product between L-Tyrosine ethylate and Damascone was prepared using the procedure described as follows:



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a)- L-Tyrosine ethyl ester (2.09 g) and Damascone (1.92 g) in  $\text{CH}_2\text{Cl}_2$  (10 ml) and molecular sieves (4Å, 5 g) were mixed together with stirring. The reaction between L-Tyrosine ethyl ester and Damascone in  $\text{CH}_2\text{Cl}_2$  and molecular sieves is followed with mass spectroscopy. After 24 hours, formation of the  $\beta$ -aminoketone has been found. The solvent is evaporated and a viscous liquid is obtained. The NMR shows small amounts of unreacted Damascone (8%).

b)- L-Tyrosine ethyl ester (2.09 g) and Damascone (1.92 g) in  $\text{CH}_2\text{Cl}_2$  (10 ml) were mixed together with stirring. The reaction between L-Tyrosine ethyl ester and Damascone in  $\text{CH}_2\text{Cl}_2$  is followed with mass spectroscopy. After 24h formation of  $\beta$ -aminoketone is observed. The solvent is evaporated and a viscous oil is obtained. The NMR shows small amounts of unreacted Damascone (6%).

[0217] Similarly, the synthesis between Hexyl Cinnamic Aldehyde and L-Tyrosine ethyl ester is performed according to either of the methods above described.

[0218] In the following formulation examples all levels are quoted as % by weight of the composition unless otherwise stated, and incorporation of the amine reaction product so called herein after "ARP" in the fully formulated composition is carried out by dry addition (d), spray on (s), encapsulation in starch (es) as described in GB-1,464,616 or cyclodextrin (ec) or as is in the composition as defined herein before. The term in bracket for the ARP in the formulation examples refers to the means of incorporation. When none is provided, the incorporation is made as it is.

### Example 1

[0219] The following high density granular laundry detergent compositions A to F were prepared in accord with the invention:



	A	B	C	D	E	F
LAS	8.0	8.0	8.0	2.0	6.0	6.0
TAS	-	0.5	-	0.5	1.0	0.1
C46(S)AS	2.0	2.5	-	-	-	-
C25AS	-	-	-	7.0	4.5	5.5
C68AS	2.0	5.0	7.0	-	-	-
C25E5	-	-	3.4	10.0	4.6	4.6
C25E7	3.4	3.4	1.0	-	-	-
C25E3S	-	-	-	2.0	5.0	4.5
QAS	-	0.8	-	-	-	-
QAS (I)	-	-	-	0.8	0.5	1.0
Zeolite A	18.1	18.0	14.1	18.1	20.0	18.1
Citric acid	-	-	-	2.5	-	2.5
Carbonate	13.0	13.0	27.0	10.0	10.0	13.0
SKS-6	-	-	-	10.0	-	10.0
Silicate	1.4	1.4	3.0	0.3	0.5	0.3
Citrate	-	1.0	-	3.0	-	-
Sulfate	26.1	26.1	26.1	6.0	-	-
Mg sulfate	0.3	-	-	0.2	-	0.2
MA/AA	0.3	0.3	0.3	4.0	1.0	1.0
CMC	0.2	0.2	0.2	0.2	0.4	0.4
PB4	9.0	9.0	5.0	-	-	-

	A	B	C	D	E	F
Percarbonate	-	-	-	-	18.0	18.0
TAED	1.5	0.4	1.5	-	3.9	4.2
NAC-OBS	-	2.0	1.0	-	-	-
DTPMP	0.25	0.25	0.25	0.25	-	-
SRP 2	-	-	-	0.2	-	0.2
EDDS	-	0.25	0.4	-	0.5	0.5
CFAA	-	1.0	-	2.0	-	-
HEDP	0.3	0.3	0.3	0.3	0.4	0.4
QEA	-	-	-	0.2	-	0.5
Protease I	-	-	0.26	1.0	-	-
Protease	0.26	0.26	-	-	1.5	1.0
Cellulase	0.3	-	-	0.3	0.3	0.3
Amylase	0.1	0.1	0.1	0.4	0.5	0.5
Lipase (1)	0.3	-	-	0.5	0.5	0.5
Photoactivated bleach (ppm)	15 ppm	15 ppm	15 ppm	-	20 ppm	20 ppm
PVNO/PVPVI	-	-	-	0.1	-	-
Brightener 1	0.09	0.09	0.09	-	0.09	0.09
Perfume spray on	0.3	0.3	0.3	0.4	0.4	0.4
ARP 1	0.3(d)	0.1(es)	-	-	0.1(d)	0.5(ec)
ARP 2	-	-	0.04(s)	0.04(ec)	0.02(s)	-
Silicone antifoam	0.5	0.5	0.5	-	0.3	0.3
Misc/minors to 100%						
Density in g/litre	850	850	850	850	850	850

**Example 2**

[0220] The following granular laundry detergent compositions G to L of particular utility under European machine wash conditions were prepared in accord with the invention:

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	G	H	I	J	K	L
LAS	5.5	7.5	5.0	5.0	6.0	7.0
TAS	1.25	1.86	-	0.8	0.4	0.3
C24AS/C25AS	-	2.24	5.0	5.0	5.0	2.2
C25E3S	-	0.76	1.0	1.5	3.0	1.0
C45E7	3.25	-	-	-	-	3.0
TFAA	-	-	2.0	-	-	-
C25E5	-	5.5	-	-	-	-
QAS	0.8	-	-	-	-	-
QAS II	-	0.7	1.0	0.5	1.0	0.7
STPP	19.7	-	-	-	-	-
Zeolite A	-	19.5	25.0	19.5	20.0	17.0
NaSKS-6/citric acid (79:21)	-	10.6	-	10.6	-	-
NaSKS-6	-	-	9.0	-	10.0	10.0
Carbonate	6.1	21.4	9.0	10.0	10.0	18.0
Bicarbonate	-	2.0	7.0	5.0	-	2.0
Silicate	6.8	-	-	0.3	0.5	-
Citrate	-	-	4.0	4.0	-	-
Sulfate	39.8	-	-	5.0	-	12.0
Mg sulfate	-	-	0.1	0.2	0.2	-
MA/AA	0.5	1.6	3.0	4.0	1.0	1.0
CMC	0.2	0.4	1.0	1.0	0.4	0.4
PB4	5.0	12.7	-	-	-	-
Percarbonate	-	-	-	-	18.0	15.0
TAED	0.5	3.1	-	-	5.0	-

	G	H	I	J	K	L
NAC-OBS	1.0	3.5	-	-	-	2.5
DTPMP	0.25	0.2	0.3	0.4	-	0.2
HEDP	-	0.3	-	0.3	0.3	0.3
QEA	-	-	1.0	1.0	1.0	-
Protease I	-	-	-	0.5	1.2	-
Protease	0.26	0.85	0.9	1.0	-	0.7
Lipase (1)	0.15	0.15	0.3	0.3	0.3	0.2
Cellulase	0.28	0.28	0.2	0.2	0.3	0.3
Amylase	0.1	0.1	0.4	0.4	0.6	0.2
PVNO/PVPVI	-	-	0.2	0.2	-	-
PVP	0.9	1.3	-	-	-	0.9
SRP 1	-	-	0.2	0.2	0.2	-
Photoactivated bleach (1) (ppm)	15 ppm	27 ppm	-	-	20 ppm	20 ppm
Photoactivated bleach (2) (ppm)	15 ppm	-	-	-	-	-
Brightener 1	0.08	0.19	-	-	0.09	0.15
Brightener 2	-	0.04	-	-	-	-
Perfume	0.3	0.3	0.4	0.3	0.4	0.3
ARP1	0.1(d) 0.1(es)	1.0(d)	-	-	-	0.1(es)
ARP2	-	-	0.04(s)	0.02(ec)	0.04(d)	0.02(es)
Silicone antifoam	0.5	2.4	0.3	0.5	0.3	2.0
Minors/misc to 100%						
Density in g/litre	750	750	750	750	750	750

**Example 3**

[0221] The following detergent formulations of particular utility under European machine wash conditions were prepared in accord with the invention.

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	M	N	O	P
Blown powder				
LAS	6.0	5.0	11.0	6.0
TAS	2.0	-	-	2.0
Zeolite A	24.0	-	-	20.0
STPP	-	27.0	24.0	-
Sulfate	4.0	6.0	13.0	-
MA/AA	1.0	4.0	6.0	2.0
Silicate	1.0	7.0	3.0	3.0
CMC	1.0	1.0	0.5	0.6
Brightener 1	0.2	0.2	0.2	0.2
Silicone antifoam	1.0	1.0	1.0	0.3
DTPMP	0.4	0.4	0.2	0.4
Spray on				
Brightener	0.02	-	-	0.02
C45E7	-	-	-	5.0
C45E2	2.5	2.5	2.0	-
C45E3	2.6	2.5	2.0	-
Perfume	0.5	0.3	0.5	0.2
Silicone antifoam	0.3	0.3	0.3	-
Dry additives				
QEA	-	-	-	1.0
EDDS	0.3	-	-	-
Sulfate	2.0	3.0	5.0	10.0
Carbonate	6.0	13.0	15.0	14.0
Citric acid	2.5	-	-	2.0
QAS II	0.5	-	-	0.5
SKS-6	10.0	-	-	-
Percarbonate	18.5	-	-	-
PB4	-	18.0	10.0	21.5
TAED	2.0	2.0	-	2.0
NAC-OBS	3.0	2.0	4.0	-
Protease	1.0	1.0	1.0	1.0
Lipase	-	0.4	-	0.2
Lipase (1)	0.4	-	0.4	-
Amylase	0.2	0.2	0.2	0.4
Brightener 1	0.05	-	-	0.05
ARP3	0.3	0.1(es)	1.0	0.1
				0.05(ec)
Misc/minor to 100%-				

**Example 4**

**[0222]** The following granular detergent formulations were prepared in accord with the invention.

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	Q	R	S	T	U	V
Blown powder						
LAS	23.0	8.0	7.0	9.0	7.0	7.0
TAS	-	-	-	-	1.0	-
C45AS	6.0	6.0	5.0	8.0	-	-
C45AES	-	1.0	1.0	1.0	-	-
C45E35	-	-	-	-	2.0	4.0
Zeolite A	10.0	18.0	14.0	12.0	10.0	10.0
MA/AA	-	0.5	-	-	-	2.0

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	Q	R	S	T	U	V
MA/AA (1)	7.0	-	-	-	-	-
AA	-	3.0	3.0	2.0	3.0	3.0
Sulfate	5.0	6.3	14.3	11.0	15.0	19.3
Silicate	10.0	1.0	1.0	1.0	1.0	1.0
Carbonate	15.0	20.0	10.0	20.7	8.0	6.0
PEG 4000	0.4	1.5	1.5	1.0	1.0	1.0
DTPA	-	0.9	0.5	-	-	0.5
Brightener 2	0.3	0.2	0.3	-	0.1	0.3
Spray on						
C45E7	-	2.0	-	-	2.0	2.0
C25E9	3.0	-	-	-	-	-
C23E9	-	-	1.5	2.0	-	2.0
Perfume	0.3	0.3	0.3	2.0	0.3	0.3
ARP5	0.1(s)	0.05(s)	-	-	-	-
Agglomerates						
C45AS	-	5.0	5.0	2.0	-	5.0
LAS	-	2.0	2.0	-	-	2.0
Zeolite A	-	7.5	7.5	8.0	-	7.5
Carbonate	-	4.0	4.0	5.0	-	4.0
PEG 4000	-	0.5	0.5	-	-	0.5
Misc (water etc)	-	2.0	2.0	2.0	-	2.0
Dry additives						
QAS (I)	-	-	-	-	1.0	-
Citric acid	-	-	-	-	2.0	-
PB4	-	-	-	-	12.0	1.0
PB1	4.0	1.0	3.0	2.0	-	-
Percarbonate	-	-	-	-	2.0	10.0
Carbonate	-	5.3	1.8	-	4.0	4.0
NOBS	4.0	-	6.0	-	-	0.6
Methyl cellulose	0.2	-	-	-	-	-

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	Q	R	S	T	U	V
SKS-6	8.0	-	-	-	-	-
STS	-	-	2.0	-	1.0	-
Cumene sulfonic acid	-	1.0	-	-	-	2.0
Lipase	0.2	-	0.2	-	0.2	0.4
Cellulase	0.2	0.2	0.2	0.3	0.2	0.2
Amylase	0.2	-	0.1	-	0.2	-
Protease	0.5	0.5	0.5	0.3	0.5	0.5
PVPVI	-	-	-	-	0.5	0.1
PVP	-	-	-	-	0.5	-
PVNO	-	-	0.5	0.3	-	-
QEA	-	-	-	-	1.0	-
SRP1	0.2	0.5	0.3	-	0.2	-
ARP2	-	-	0.04(d)	0.02	0.01(es)	0.02(es)
Silicone antifoam	0.2	0.4	0.2	0.4	0.1	-
Mg sulfate	-	-	0.2	-	0.2	-
Misc/minors to 100%						

**Example 5**

[0223] The following nil bleach-containing detergent formulations of particular use in the washing of coloured clothing, according to the present invention were prepared:

	W	X	Y
Blown Powder			
Zeolite A	15.0	15.0	-
Sulfate	0.0	5.0	-
LAS	3.0	3.0	-
DTPMP	0.4	0.5	-
CMC	0.4	0.4	-
MA/AA	4.0	4.0	-
Agglomerates			
C45AS	-	-	11.0
LAS	6.0	5.0	-
TAS	3.0	2.0	-
Silicate	4.0	4.0	-
Zeolite A	10.0	15.0	13.0
CMC	-	-	0.5
MA/AA	-	-	2.0
Carbonate	9.0	7.0	7.0



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	W	X	Y
Spray On			
Perfume	0.3	0.3	0.5
C45E7	4.0	4.0	4.0
C25E3	2.0	2.0	2.0
ARP2	0.04(s)	-	-
Dry additives			
MA/AA	-	-	3.0
NaSKS-6	-	-	12.0
Citrate	10.0	-	8.0
Bicarbonate	7.0	3.0	5.0
Carbonate	8.0	5.0	7.0
PVPVI/PVNO	0.5	0.5	0.5
Alcalase	0.5	0.3	0.9
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
ARP1	-	0.3	0.1(es)
Silicone antifoam	5.0	5.0	5.0
Dry additives			
Sulfate	0.0	9.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	700	700	700

**Example 6**

[0224] The following granular detergent formulations were prepared in accord with the invention.

	Z	AA	BB	CC
Base granule				
Zeolite A	30.0	22.0	24.0	10.0
Sulfate	10.0	5.0	10.0	7.0
MA/AA	3.0	-	-	-
AA	-	1.6	2.0	-
MA/AA (1)	-	12.0	-	6.0
LAS	14.0	10.0	9.0	20.0
C45AS	8.0	7.0	9.0	7.0
C45AES	-	1.0	1.0	-
Silicate	-	1.0	0.5	10.0
Soap	-	2.0	-	-
Brightener 1	0.2	0.2	0.2	0.2
Carbonate	6.0	9.0	10.0	10.0
PEG 4000	-	1.0	1.5	-
DTPA	-	0.4	-	-
Spray on				
C25E9	-	-	-	5.0
C45E7	1.0	1.0	-	-
C23E9	-	1.0	2.5	-
Perfume	0.2	0.3	0.3	-
ARP2	0.04(s)	-	-	-

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	<b>Z</b>	<b>AA</b>	<b>BB</b>	<b>CC</b>
<b>Dry additives</b>				
Carbonate	5.0	10.0	18.0	8.0
PVPVI/PVNO	0.5	-	0.3	-
Protease	1.0	1.0	1.0	0.5
Lipase	0.4	-	-	0.4
Amylase	0.1	-	-	0.1
Cellulase	0.1	0.2	0.2	0.1
NOBS	-	4.0	-	4.5
PB1	1.0	5.0	1.5	6.0
Sulfate	4.0	5.0	-	5.0
SRPI	-	0.4	-	-
ARP1	-	0.3	0.1(es)	-
ARP2	-	-	-	0.02(es)
Sud supressor	-	0.5	0.5	-
Misc/minor to 100%				

**Example 7**

**[0225]** The following granular detergent compositions were prepared in accord with the invention.

	<b>DD</b>	<b>EE</b>	<b>FF</b>
<b>Blown powder</b>			
Zeolite A	20.0	-	15.0
STPP	-	20.0	-
Sulphate	-	-	5.0
Carbonate	-	-	5.0
TAS	-	-	1.0
LAS	6.0	6.0	6.0
C68AS	2.0	2.0	-
Silicate	3.0	8.0	-
MA/AA	4.0	2.0	2.0
CMC	0.6	0.6	0.2
Brightener 1	0.2	0.2	0.1
DTPMP	0.4	0.4	0.1
STS	-	-	1.0
<b>Spray on</b>			
C45E7	5.0	5.0	4.0
Silicone antifoam	0.3	0.3	0.1
Perfume	0.2	0.2	0.3
ARP5	0.1(s)	0.05(s)	0.08(s)
<b>Dry additives</b>			
QEA	-	-	1.0
Carbonate	14.0	9.0	10.0
PB1	1.5	2.0	-
PB4	18.5	13.0	13.0
TAED	2.0	2.0	2.0
QAS (I)	-	-	1.0
Photoactivated bleach	15 ppm	15 ppm	15ppm
SKS-6	-	-	3.0

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	DD	EE	FF
Dry additives			
Protease	1.0	1.0	0.2
Lipase	0.2	0.2	0.2
Amylase	0.4	0.4	0.2
Cellulase	0.1	0.1	0.2
Sulfate	10.0	20.0	5.0
Misc/minors to 100%			
Density (g/litre)	700	700	700

**Example 8**

[0226] The following detergent compositions, according to the present invention were prepared:

	GG	HH	II
Blown Powder			
Zeolite A	15.0	15.0	15.0
Sulfate	0.0	5.0	0.0
LAS	3.0	3.0	3.0
QAS	-	1.5	1.5
DTPMP	0.4	0.2	0.4
EDDS	-	0.4	0.2
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Agglomerates			
LAS	5.0	5.0	5.0
TAS	2.0	2.0	1.0
Silicate	3.0	3.0	4.0
Zeolite A	8.0	8.0	8.0
Carbonate	8.0	8.0	4.0
Spray On			
Perfume	0.3	0.3	0.3
C45E7	2.0	2.0	2.0
C25E3	2.0	-	-
ARP2	0.02(s)	-	-
Dry additives			
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-
Carbonate	8.0	15.0	10.0
TAED	6.0	2.0	5.0
PB1	14.0	7.0	10.0
PEO	-	-	0.2
ARP1	-	0.2	0.08(ec)
Bentonite clay	-	-	10.0
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Silicone antifoam	5.0	5.0	5.0
Dry additives			

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	GG	HH	II
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Misc/minors to 100%	100.0	100.0	100.0
Density (g/litre)	850	850	850

**Example 9**

[0227] The following detergent formulations, according to the present invention were prepared:

	JJ	KK	LL	MM
LAS	18.0	14.0	24.0	20.0
QAS	0.7	1.0	-	0.7
TFAA	-	1.0	-	-
C23E56.5	-	-	1.0	-
C45E7	-	1.0	-	-
C45E3S	1.0	2.5	1.0	-
STPP	32.0	18.0	30.0	22.0
Silicate	9.0	5.0	9.0	8.0
Carbonate	11.0	7.5	10.0	5.0
Bicarbonate	-	7.5	-	-
PB1	3.0	1.0	-	-
PB4	-	1.0	-	-
NOBS	2.0	1.0	-	-
DTPMP	-	1.0	-	-
DTPA	0.5	-	0.2	0.3
SRP 1	0.3	0.2	-	0.1
MA/AA	1.0	1.5	2.0	0.5
CMC	0.8	0.4	0.4	0.2
PEI	-	-	0.4	-
Sodium sulfate	20.0	10.0	20.0	30.0
Mg sulfate	0.2	-	0.4	0.9
Protease	0.8	1.0	0.5	0.5
Amylase	0.5	0.4	-	0.25
Lipase	0.2	-	0.1	-
Cellulase	0.15	-	-	0.05
Photoactivated bleach (ppm)	30ppm	20ppm	-	10ppm
ARP4	0.04(s)	0.02(ec)	0.1(s)	0.01(es)
Perfume spray on	0.3	0.3	0.1	0.2
Brightener 1/2	0.05	0.2	0.08	0.1
Misc/minors to 100%				

**Example 10**

[0228] The following liquid detergent formulations were prepared in accord with the invention (levels are given as parts per weight).

	NN	OO	PP	QQ	RR
LAS	11.5	8.8	-	3.9	-

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	NN	OO	PP	QQ	RR
C25E2.5S	-	3.0	18.0	-	16.0
C45E2.25S	11.5	3.0	-	15.7	-
C23E9	-	2.7	1.8	2.0	1.0
C23E7	3.2	-	-	-	-
CFAA	-	-	5.2	-	3.1
TPKFA	1.6	-	2.0	0.5	2.0
Citric acid (50%)	6.5	1.2	2.5	4.4	2.5
Calcium formate	0.1	0.06	0.1	-	-
Sodium formate	0.5	0.06	0.1	0.05	0.05
Sodium cumene sulfonate	4.0	1.0	3.0	1.18	-
Borate	0.6	-	3.0	2.0	2.9
Sodium hydroxide	5.8	2.0	3.5	3.7	2.7
Ethanol	1.75	1.0	3.6	4.2	2.9
1,2 propanediol	3.3	2.0	8.0	7.9	5.3
Monoethanolamine	3.0	1.5	1.3	2.5	0.8
TEPAE	1.6	-	1.3	1.2	1.2
Protease	1.0	0.3	1.0	0.5	0.7
Lipase	-	-	0.1	-	-
Cellulase	-	-	0.1	0.2	0.05
Amylase	-	-	-	0.1	-
SRP1	0.2	-	0.1	-	-
DTPA	-	-	0.3	-	-
PVNO	-	-	0.3	-	0.2
ARP1	0.3	-	-	-	-
ARP2	-	0.04	-	-	-
ARP3	-	-	0.3	-	-
ARP4	-	-	-	0.04	-
ARP5	-	-	-	-	0.1
Brightener 1	0.2	0.07	0.1	-	-
Silicone antifoam	0.04	0.02	0.1	0.1	0.1
Water/minors					

**Example 11**

[0229] The following liquid detergent formulations were prepared in accord with the invention (levels are given in parts per weight):

	SS	TT	UU	VV	WW	XX	YY	ZZ
LAS	10.0	13.0	9.0	-	25.0	-	-	-
C25AS	4.0	1.0	2.0	10.0	-	13.0	18.0	15.0
C25E3S	1.0	-	-	3.0	-	2.0	2.0	4.0
C25E7	6.0	8.0	13.0	2.5	-	-	4.0	4.0
TFAA	-	-	-	4.5	-	6.0	8.0	8.0
APA	-	1.4	-	-	3.0	1.0	2.0	-
TPKFA	2.0	-	13.0	7.0	-	15.0	11.0	11.0
Citric acid	2.0	3.0	1.0	1.5	1.0	1.0	1.0	1.0
Dodecenyl/tetradecenyl succinic acid	12.0	10.0	-	-	15.0	-	-	-
Rape seed fatty acid	4.0	2.0	1.0	-	1.0	-	3.5	-
Ethanol	4.0	4.0	7.0	2.0	7.0	2.0	3.0	2.0

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	SS	TT	UU	VV	WW	XX	YY	ZZ
1,2 Propanediol	4.0	4.0	2.0	7.0	6.0	8.0	10.0	13.0
Monoethanolamine	-	-	-	5.0	-	-	9.0	9.0
Triethanolamine	-	-	8.0	-	-	-	-	-
TEPAE	0.5	-	0.5	0.2	-	-	0.4	0.3
DTPMP	1.0	1.0	0.5	1.0	2.0	1.2	1.0	-
Protease	0.5	0.5	0.4	0.25	-	0.5	0.3	0.6
Alcalase	-	-	-	-	1.5	-	-	-
Lipase	-	0.10	-	0.01	-	-	0.15	0.15
Amylase	0.25	0.25	0.6	0.5	0.25	0.9	0.6	0.6
Cellulase	-	-	-	0.05	-	-	0.15	0.15
Endolase	-	-	-	0.10	-	-	0.07	-
SRP2	0.3	-	0.3	0.1	-	-	0.2	0.1
Boric acid	0.1	0.2	1.0	2.0	1.0	1.5	2.5	2.5
Calcium chloride	-	0.02	-	0.01	-	-	-	-
Bentonite clay	-	-	-	-	4.0	4.0	-	-
Brightener 1	-	0.4	-	-	0.1	0.2	0.3	-
Sud supressor	0.1	0.3	-	0.1	0.4	-	-	-
Opacifier	0.5	0.4	-	0.3	0.8	0.7	-	-
ARP1	0.3	-	0.1	-	0.05	-	0.1	0.08
ARP2	-	0.04	-	0.02	-	0.1	0.02	0.1
Water/minors								
NaOH up to pH	8.0	8.0	7.6	7.7	8.0	7.5	8.0	8.2

**Example 12**

**[0230]** The following liquid detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

	AB	AC
LAS	27.6	18.9
C45AS	13.8	5.9
C13E8	3.0	3.1
Oleic acid	3.4	2.5
Citric acid	5.4	5.4
Sodium hydroxide	0.4	3.6
Calcium formate	0.2	0.1
Sodium formate	-	0.5
Ethanol	7.0	-
Monoethanolamine	16.5	8.0
1,2 propanediol	5.9	5.5
Xylene sulfonic acid	-	2.4
TEPAE	1.5	0.8
Protease	1.5	0.6
PEG	-	0.7
Brightener 2	0.4	0.1
Perfume spray on	0.5	0.3
ARP1	0.3	-
ARP4	-	0.04
Water/minors		

**Example 13**

[0231] The following laundry bar detergent compositions were prepared in accord with the invention (levels are given in parts per weight).

	AD	AE	AF	AG	AH	AI	AJ	AK
LAS	-	-	19.0	15.0	21.0	6.75	8.8	-
C28AS	30.0	13.5	-	-	-	15.75	11.2	22.5
Sodium laurate	2.5	9.0	-	-	-	-	-	-
Zeolite A	2.0	1.25	-	-	-	1.25	1.25	1.25
Carbonate	20.0	3.0	13.0	8.0	10.0	15.0	15.0	10.0
Calcium carbonate	27.5	39.0	35.0	-	-	40.0	-	40.0
Sulfate	5.0	5.0	3.0	5.0	3.0	-	-	5.0
TSPP	5.0	-	-	-	-	5.0	2.5	-
STPP	5.0	15.0	10.0	-	-	7.0	8.0	10.0
Bentonite clay	-	10.0	-	-	5.0	-	-	-
DTPMP	-	0.7	0.6	-	0.6	0.7	0.7	0.7
CMC	-	1.0	1.0	1.0	1.0	-	-	1.0
Talc	-	-	10.0	15.0	10.0	-	-	-
Silicate	-	-	4.0	5.0	3.0	-	-	-
PVNO	0.02	0.03	-	0.01	-	0.02	-	-
MA/AA	0.4	1.0	-	-	0.2	0.4	0.5	0.4
SRP1	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Protease	-	0.12	-	0.08	0.08	-	-	0.1
Lipase	-	0.1	-	0.1	-	-	-	-
Amylase	-	-	0.8	-	-	-	0.1	-
Cellulase	-	0.15	-	-	0.15	0.1	-	-
PEO	-	0.2	-	0.2	0.3	-	-	0.3
Perfume	1.0	0.5	0.3	0.2	0.4	-	-	0.4
Mg sulfate	-	-	3.0	3.0	3.0	-	-	-
ARP1	0.3	-	-	-	-	0.5	-	-
ARP2	-	0.04	-	-	-	-	0.08	-
ARP3	-	-	0.3	-	-	-	-	-
ARP4	-	-	-	0.04	-	-	-	-
ARP5	-	-	-	-	0.1	-	-	0.05
Brightener	0.15	0.10	0.15	-	-	-	-	0.1
Photoactivated bleach (ppm)	-	15.0	15.0	15.0	15.0	-	-	15.0

**Example 14**

[0232] The following detergent additive compositions were prepared according to the present invention :

	AL	AM	AN
LAS	-	5.0	5.0
STPP	30.0	-	20.0
Zeolite A	-	35.0	20.0
PB1	20.0	15.0	-
TAED	10.0	8.0	-
ARP1	0.3	-	0.1

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	AL	AM	AN
ARP2	-	0.04	0.02
Protease	-	0.3	0.3
Amylase	-	0.06	0.06
Minors, water and miscellaneous			Up to 100%

**Example 15**

[0233] The following compact high density (0.96Kg/l) dishwashing detergent compositions were prepared according to the present invention :

	AO	AP	AQ	AR	AS	AT	AU	AV
STPP	-	-	54.3	51.4	51.4	-	-	50.9
Citrate	35.0	17.0	-	-	-	46.1	40.2	-
Carbonate	-	17.5	14.0	14.0	14.0	-	8.0	32.1
Bicarbonate	-	-	-	-	-	25.4	-	-
Silicate	32.0	14.8	14.8	10.0	10.0	1.0	25.0	3.1
Metasilicate	-	2.5	-	9.0	9.0	-	-	-
PB1	1.9	9.7	7.8	7.8	7.8	-	-	-
PB4	8.6	-	-	-	-	-	-	-
Percarbonate	-	-	-	-	-	6.7	11.8	4.8
Nonionic	1.5	2.0	1.5	1.7	1.5	2.6	1.9	5.3
TAED	5.2	2.4	-	-	-	2.2	-	1.4
HEDP	-	1.0	-	-	-	-	-	-
DTPMP	-	0.6	-	-	-	-	-	-
MnTACN	-	-	-	-	-	-	0.008	-
PAAC	-	-	0.008	0.01	0.007	-	-	-
BzP	-	-	-	-	1.4	-	-	-
Paraffin	0.5	0.5	0.5	0.5	0.5	0.6	-	-
ARP3	0.1	0.3	0.2	0.05	-	-	-	0.8
ARP1	-	-	-	-	0.3	0.03	0.5	-
Protease	0.072	0.072	0.029	0.053	0.046	0.026	0.059	0.06
Amylase	0.012	0.012	0.006	0.012	0.013	0.009	0.017	0.03
Lipase	-	0.001	-	0.005	-	-	-	-
BTA	0.3	0.3	0.3	0.3	0.3	-	0.3	0.3
MA/AA	-	-	-	-	-	-	4.2	-
480N	3.3	6.0	-	-	-	-	-	0.9
Perfume	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.1
Sulphate	7.0	20.0	5.0	2.2	0.8	12.0	4.6	-
pH	10.8	11.0	10.8	11.3	11.3	9.6	10.8	10.9
Miscellaneous and water			Up to 100%					

**Example 16**

[0234] The following granular dishwashing detergent compositions of bulk density 1.02Kg/L were prepared according to the present invention:



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	AW	AX	AY	AZ	BA	BC	BD	BE
STPP	30.0	30.0	33.0	34.2	29.6	31.1	26.6	17.6
Carbonate	30.5	30.5	31.0	30.0	23.0	39.4	4.2	45.0
Silicate	7.4	7.4	7.5	7.2	13.3	3.4	43.7	12.4
Metasilicate	-	-	4.5	5.1	-	-	-	-
Percarbonate	-	-	-	-	-	4.0	-	-
PB1	4.4	4.2	4.5	4.5	-	-	-	-
NADCC	-	-	-	-	2.0	-	1.6	1.0
Nonionic	1.2	1.0	0.7	0.8	1.9	0.7	0.6	0.3
TAED	1.0	-	-	-	-	0.8	-	-
PAAC	-	0.004	0.004	0.004	-	-	-	-
BzP	-	-	-	1.4	-	-	-	-
Paraffin	0.25	0.25	0.25	0.25	-	-	-	-
ARP3	0.3	0.1(ec)	0.8	0.2(es)	-	-	0.1(ec)	0.2
ARP1	-	-	-	-	0.3	0.1(ec)	0.1(ec)	0.2
Protease	0.036	0.015	0.03	0.028	-	0.03	-	-
Amylase	0.003	0.003	0.01	0.006	-	0.01	-	-
Lipase	0.005	-	0.001	-	-	-	-	-
BTA	0.15	0.15	0.15	0.15	-	-	-	-
Perfume	0.2	0.2	0.2	0.2	0.1	0.2	0.2	-
Sulphate	23.4	25.0	22.0	18.5	30.1	19.3	23.1	23.6
pH	10.8	10.8	11.3	11.3	10.7	11.5	12.7	10.9
Miscellaneous and water Up to 100%								

**Example 17**

[0235] The following tablet detergent compositions were prepared according to the present invention by compression of a granular dishwashing detergent composition at a pressure of 13KN/cm<sup>2</sup><sub>a</sub> using a standard 12 head rotary press:

	BF	BJ	BK	BL	BM	BN
STPP	-	48.8	49.2	38.0	-	46.8
Citrate	26.4	-	-	-	31.1	-
Carbonate	-	5.0	14.0	15.4	14.4	23.0
Silicate	26.4	14.8	15.0	12.6	17.7	2.4
ARP1	0.3	-	-	-	0.06	-
ARP2	-	0.04	-	-	-	0.08
ARP3	-	-	0.3	0.1(ec)	-	-
Protease	0.058	0.072	0.041	0.033	0.052	0.013
Amylase	0.01	0.03	0.012	0.007	0.016	0.002
Lipase	0.005	-	-	-	-	-
PB1	1.6	7.7	12.2	10.6	15.7	-
PB4	6.9	-	-	-	-	14.4
Nonionic	1.5	2.0	1.5	1.65	0.8	6.3
PAAC	-	-	0.02	0.009	-	-
MnTACN	-	-	-	-	0.007	-
TAED	4.3	2.5	-	-	1.3	1.8
HEDP	0.7	-	-	0.7	-	0.4
DTPMP	0.65	-	-	-	-	-
Paraffin	0.4	0.5	0.5	0.55	-	-

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	BF	BJ	BK	BL	BM	BN
BTA	0.2	0.3	0.3	0.3	-	-
PA30	3.2	-	-	-	-	-
MA/AA	-	-	-	-	4.5	0.55
Perfume	-	-	0.05	0.05	0.2	0.2
Sulphate	24.0	13.0	2.3	-	10.7	3.4
Weight of tablet	25g	25g	20g	30g	18g	20g
pH	10.6	10.6	10.7	10.7	10.9	11.2
Miscellaneous and water		Up to 100%				

**Example 18**

[0236] The following liquid dishwashing detergent compositions of density 1.40Kg/L were prepared according to the present invention :

	BO	BP	BQ	BR
STPP	17.5	17.5	17.2	16.0
Carbonate	2.0	-	2.4	-
Silicate	5.3	6.1	14.6	15.7
NaOCl	1.15	1.15	1.15	1.25
Polygen/carbopol	1.1	1.0	1.1	1.25
Nonionic	-	-	0.1	-
NaBz	0.75	0.75	-	-
ARP3	0.3	0.5	0.05	0.1
NaOH	-	1.9	-	3.5
KOH	2.8	3.5	3.0	-
pH	11.0	11.7	10.9	11.0
Sulphate, miscellaneous and water		up to 100%		

**Example 19**

[0237] The following liquid rinse aid compositions were prepared according to the present invention :

	BS	BT	BU
Nonionic	12.0	-	14.5
Nonionic blend	-	64.0	-
Citric	3.2	-	6.5
HEDP	0.5	-	-
PEG	-	5.0	-
SCS	4.8	-	7.0
Ethanol	6.0	8.0	-
ARP1	0.3	-	0.1
ARP2	-	0.04	0.01
pH of the liquid	2.0	7.5	/
Miscellaneous and water		Up to 100%	

**Example 20**

[0238] The following liquid dishwashing compositions were prepared according to the present invention :

	BV	BW	BX	BY	BZ
C17ES	28.5	27.4	19.2	34.1	34.1
Amine oxide	2.6	5.0	2.0	3.0	3.0
C12 glucose amide	-	-	6.0	-	-
Betaine	0.9	-	-	2.0	2.0
Xylene sulfonate	2.0	4.0	-	2.0	-
Neodol C11E9	-	-	5.0	-	-
Polyhydroxy fatty acid amide	-	-	-	6.5	6.5
Sodium diethylene penta acetate (40%)	-	-	0.03	-	-
TAED	-	-	-	0.06	0.06
Sucrose	-	-	-	1.5	1.5
Ethanol	4.0	5.5	5.5	9.1	9.1
Alkyl diphenyl oxide disulfonate	-	-	-	-	2.3
Ca formate	-	-	-	0.5	1.1
Ammonium citrate	0.06	0.1	-	-	-
Na chloride	-	1.0	-	-	-
Mg chloride	3.3	-	0.7	-	-
Ca chloride	-	-	0.4	-	-
Na sulfate	-	-	0.06	-	-
Mg sulfate	0.08	-	-	-	-
Mg hydroxide	-	-	-	2.2	2.2
Na hydroxide	-	-	-	1.1	1.1
Hydrogen peroxide	200ppm	0.16	0.006	-	-
ARP3	0.3	-	0.1	-	0.1
ARP1	-	0.3	-	0.1	0.1
Protease	0.017	0.005	0.0035	0.003	0.002
Perfume	0.18	0.09	0.09	0.2	0.2
Water and minors	Up to 100%				

**Example 21**

[0239] The following liquid hard surface cleaning compositions were prepared according to the present invention :

	CA	CB	CD	CE	CF
ARP2	0.04	-	0.08	-	0.01
ARP3	-	0.3	-	0.125	0.1
Amylase	0.01	0.002	0.005	-	-
Protease	0.05	0.01	0.02	-	-
Hydrogen peroxide	-	-	-	6.0	6.8
Acetyl triethyl citrate	-	-	-	2.5	-
DTPA	-	-	-	0.2	-
Butyl hydroxy toluene	-	-	-	0.05	-
EDTA*	0.05	0.05	0.05	-	-
Citric / Citrate	2.9	2.9	2.9	1.0	-
LAS	0.5	0.5	0.5	-	-

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	CA	CB	CD	CE	CF
C12 AS	0.5	0.5	0.5	-	-
C10AS	-	-	-	-	1.7
C12(E)S	0.5	0.5	0.5	-	-
C12, 13 E6.5 nonionic	7.0	7.0	7.0	-	-
Neodol 23-6.5	-	-	-	12.0	-
Dobanol 23-3	-	-	-	-	1.5
Dobanol 91-10	-	-	-	-	1.6
C25AE1.8S	-	-	-	6.0	
Na paraffin sulphonate	-	-	-	6.0	
Perfume	1.0	1.0	1.0	0.5	0.2
Propanediol	-	-	-	1.5	
Ethoxylated tetraethylene pentamine	-	-	-	1.0	-
2, Butyl octanol	-	-	-	-	0.5
Hexyl carbitol**	1.0	1.0	1.0	-	-
SCS	1.3	1.3	1.3	-	-
pH adjusted to	7-12	7-12	7-12	4	-
Miscellaneous and water	Up to 100%				

\*Na4 ethlenediamine diacetic acid

\*\*Diethylene glycol monohexyl ether

**Example 22**

[0240] The following spray composition for cleaning of hard surfaces and removing household mildew was prepared according to the present invention :

ARP2	0.04
Amylase	0.01
Protease	0.01
Na octyl sulfate	2.0
Na dodecyl sulfate	4.0
Na hydroxide	0.8
Silicate	0.04
Butyl carbitol*	4.0
Perfume	0.35
Water/minors	up to 100%

\*Diethylene glycol monobutyl ether

**Example 23**

[0241] The following lavatory cleansing block compositions were prepared according to the present invention.

	CK	CL	CM
C16-18 fatty alcohol/50EO	80.0	-	-
LAS	-	-	80.0
Nonionic	-	1.0	-
Oleoamide surfactant	-	26.0	-
Partially esterified copolymer of vinylmethyl ether and maleic anhydride, viscosity 0.1-0.5	5.0	-	-
Polyethylene glycol MW 8000	-	39.0	-
Water-soluble K-polyacrylate MW 4000-8000	-	12.0	-

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	CK	CL	CM
Water-soluble Na-copolymer of acrylamide (70%) and acrylic acid (30%) low MW	-	19.0	-
Na triphosphate	10.0	-	-
Carbonate	-	-	8.0
ARP2	0.04	-	0.01
ARP3	-	0.25	0.1
Dye	2.5	1.0	1.0
Perfume	3.0	-	7.0
KOH / HCL solution		pH 6-11	

## Example 24

[0242] The following toilet bowl cleaning composition was prepared according to the present invention.

	CN	CO
C14-15 linear alcohol 7EO	2.0	10.0
Citric acid	10.0	5.0
ARP2	0.04	-
ARP3	-	0.1
DTPMP	-	1.0
Dye	2.0	1.0
Perfume	3.0	3.0
NaOH pH 6-11		
Water and minors	Up to 100%	

## Claims

1. A laundry and cleaning composition comprising a detergent ingredient and a product of reaction between a primary amine compound and a perfume component selected from ketone, aldehyde, and mixtures thereof, characterised in that said amine compound has an Odor Intensity Index of less than that of a 1% solution of methylantranilate in dipropylene glycol, and the product of reaction has a Dry Surface Odor Index of more than 5.
2. A composition according to Claim 1, wherein said amine compound has the following formula:
$$B-(NH_2)_n;$$
wherein B is a carrier material, and n is an index of value of at least 1.
3. A composition according to Claim 2, wherein said carrier material is selected from inorganic or organic carriers, preferably is an organic carrier.
4. A composition according to Claim 3, wherein the inorganic carrier is an amino functionalized polydi-alkylsiloxane.
5. A composition according to Claim 3, wherein said amine having organic carrier material B is selected from aminoaryl derivatives, polyamines, amino acids and derivatives, substituted amines and amides, glucamines, dendrimers, amino-substituted mono-, di-, oligo-, poly-saccharides and/or mixtures thereof.
6. A composition according to Claim 5, wherein said aminoaryl derivatives are aminobenzene derivatives, preferably alkyl or aryl esters of 4-amino benzoate compounds, preferably selected from ethyl-4-amino benzoate, phenylethyl-4-aminobenzoate, phenyl-4-aminobenzoate, 4-amino-N'-(3-aminopropyl)-benzamide, and mixtures thereof.
7. A composition according to Claim 5, wherein said polyamines are polyethyleneimines, 2,2',2''-triaminotriethylamine; 2,2'-diamino-diethylamine; 3,3'-diamino-dipropylamine, 1,3 bis aminoethylcyclohexane; poly[oxy(methyl-1,2-ethanediyl)],  $\alpha$ -(2-aminomethylethyl)- $\omega$ -(2-amino-methylethoxy)-; poly[oxy(methyl-1,2-

ethanedyl)],  $\alpha$ -hydro- $\omega$ -(2-amino-methylethoxy)-, ether with 2-ethyl-2-(hydroxymethyl)-1,3-propanediol; C12 Sternamines; and mixtures thereof.

8. A composition according to Claim 5, wherein said amine compounds are aminoacids and derivatives, preferably selected from tyrosine, tryptophane, lysine, glutamic acid, glutamine, aspartic acid, arginine, asparagine, phenylalanine, proline, glycine, serine, histidine, threonine, methionine, tyrosine ethylate or phenyl ester, tryptophane ethylate or phenyl ester, glycine methylate, and mixture thereof, more preferably selected from tyrosine, tryptophane, and mixture thereof
9. A composition according to Claim 5, wherein said amine compounds are substituted amines and amides, preferably selected from nipecotamide, N-coco-1,3-propenediamine; N-oleyl-1,3-propenediamine; N-(tallow alkyl)-1,3-propenediamine; 1,4-diamino cyclohexane; 1,2-diamino-cyclohexane; 1,12-diaminododecane, and mixtures thereof.
10. A composition according to Claim 5, wherein said amine compounds are glucamines of formula  $H_2N-CH_2-(CH(OH))_x-CH_2OH$ , wherein one or several OH-function can be substituted, and wherein x is an integer of value 3 or 4.
11. A composition according to Claim 5, wherein said amine compound is selected from polyamidoamine dendrimers, polyethylenimine and/or polypropylenimine dendrimers, and diaminobutane polyamine DAB (PA)x dendrimers with  $x = 2 \times 4$  and n being comprised between 0 and 4, and/or mixtures thereof.
12. A composition according to Claim 5, wherein said amine compound is selected from amino-substituted mono-saccharides in the acetal or ketal form of glucose, mannose, galactose and/or fructose; amino-substituted di-saccharides in the acetal or ketal form of lactose, maltose, sucrose and/or cellobiose; amino-substituted oligo-saccharides and/or amino-substituted poly-saccharides of cyclodextrin, chitosan, cellulose, starch, guaran, mannan and/or dextran; and/or mixtures thereof.
13. A composition according to Claim 12 wherein said amino-substituted mono-, di-, oligo-, poly-saccharide is selected from Amino alginate, Diamino alginate, Hexanediamine alginate, dodecanediamine alginate, 6-amino-6-deoxy cellulose, O-ethylamine cellulose, O-methylamine cellulose, 3-amino-3-deoxy cellulose, 2-amino-2 deoxy cellulose, 2,3-diamino-2,3-dideoxy cellulose, 6-[N-(1,6-hexanediamine)]-6-deoxy cellulose, 6-[N-(1, 12-dodecanediamine)]-6-deoxy cellulose, O-[methyl-(N-1,6-hexanediamine)] cellulose, O-[methyl-(N-1,12-dodecanediamine)] cellulose, 2,3-di-[N-(1,12-dodecanediamine)] cellulose, 2,3-diamino-2,3-deoxy alpha-cyclodextrin, 2,3-diamino-2,3-deoxy beta-cyclodextrin, 2,3-diamino-2,3-deoxy gamma-cyclodextrin, 6-amino-6-deoxy alpha-cyclodextrin, 6-amino-6-deoxy beta-cyclodextrin, O-ethylamino beta-cyclodextrin, 6[N-(1,6-hexanediamino)-6-deoxy alpha cyclodextrin, 6[N-(1,6-hexanediamino)-6-deoxy beta cyclodextrin, Amino dextran, N-[di-(1,6-hexanediamine)] dextran, N-[di-(1,12-dodecanediamine)] dextran, 6-amino-6-deoxy-alpha-D-galactosyl-guaran, O-ethylamino guaran, Diamino guaran, 6-amino-6-deoxy-starch, O-ethylamino starch, 2,3-diamine-2,3-dideoxy starch, N-[6-(1,6-hexanediamine)]-6-deoxy starch, N-[6-(1,12-dodecanediamine)]-6-deoxy starch, 2,3-di-[N(1,6-hexanediamine)]-2,3-dideoxy starch, and/or mixtures thereof.
14. A composition according to any one of Claims 1-13, wherein said product of reaction is preformed before incorporation into the laundry and cleaning composition.
15. A composition according to any one of Claims 1-14, wherein said product of reaction is present in an amount of from 0.0001% to 10%, preferably from 0.001% to 5%, and more preferably from 0.01% to 2%, by weight of the composition.
16. A composition according to Claims 1-15, wherein said perfume is a perfume aldehyde selected from 1-decanal, benzaldehyde, florhydral, 2,4-dimethyl-3-cyclohexen-1-carboxaldehyde; cis/trans-3,7-dimethyl-2,6-octadien-1-al; heliotropin; 2,4,6-trimethyl-3-cyclohexene-1-carboxaldehyde; 2,6-nonadienal; alpha-n-amil cinnamic aldehyde, alpha-n-hexyl cinnamic aldehyde, P.T. Bucinal, lylal, cymal, methyl nonyl acetaldehyde, hexanal, trans-2-hexenal, and mixture thereof.
17. A composition according to Claims 1-15, wherein said perfume is a perfume ketone selected from Alpha Damascone, Delta Damascone, Iso Damascone, Carvone, Gamma-Methyl-Ionone, Iso-E-Super, 2,4,4,7-Tetramethyl-oct-6-en-3-one, Benzyl Acetone, Beta Damascone, Damasconone, methyl dihydrojasmonate, methyl cedrylone, and mixtures thereof.
18. A composition according to Claims 1-15 wherein said perfume has an Odor Detection Threshold lower or equal to than 1ppm, more preferably lower than or equal to 10ppb.
19. A compositions according to Claim 18 wherein said perfume is selected from undecylenic aldehyde, undecalactone gamma, heliotropin, dodecalactone gamma, p-anisic aldehyde, para hydroxy-phenyl-butanone, cymal, benzyl acetone, ionone alpha, p.t.bucinal, damascenone, ionone beta and methyl-nonyl ketone, and/or mixtures thereof.

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20. A method of delivering residual fragrance to a surface which comprises the steps of contacting said surface with a composition as defined in any one of Claims 1-19, and thereafter contacting the treated surface with a material so that the perfume is released.

21. A method according to Claim 20, wherein said material is water.

22. Use of a compound as defined in any one of Claims 1-19, for the manufacture of a laundry and cleaning composition for delivering residual fragrance on a surface on which it is applied.

23. Use according to Claim 22, wherein said surface is a fabric.

24. Use according to Claim 22, wherein said surface is a tile and/or ceramic.



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Application Number  
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The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>25 October 1999</b>	Examiner <b>Loiselet-Talsne, S</b>
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 98 87 0226

DOCUMENTS CONSIDERED TO BE RELEVANT			
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THE HAGUE		25 October 1999	Loiselet-Taisne, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone</p> <p>Y : particularly relevant if combined with another document of the same category</p> <p>A : technological background</p> <p>O : non-written disclosure</p> <p>P : intermediate document</p> <p>T : theory or principle underlying the invention</p> <p>E : earlier patent document, but published on, or after the filing date</p> <p>D : document cited in the application</p> <p>L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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